

(4, 5-c)FUROTROPYLIDENE - -
A TEN-PI-ELECTRON CARBENE

By
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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
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1973

DEDICATION

This work is dedicated to the past for my parents, to the present for my wife, and to the future for my children.

ACKNOWLEDGMENT

I would like to express my sincere gratitude to Professor W. M. Jones and all the members of my supervisory committee for their scholarly guidance during the preparation of this work. A special debt is owed to Dr. R. W. King of the University of Florida who good-naturedly suffered all of my questions about molecular spectroscopy. It is such men as these who keep teaching in its honored place among the professions.

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PREFACE

"Tom he said . . . the trouble about arguments is, they ain't nothing but theories, after all, and theories don't prove nothing, they only give you a place to rest on, a spell, when you are tuckered out butting around and around trying to find out something there ain't no way to find out. "

Huckleberry Finn in
"Tom Sawyer Abroad"
by Mark Twain

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Abstract of Dissertation Presented to the
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Thomas Howard Ledford

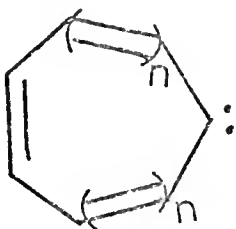
August, 1973

Chairman: Professor William M. Jones, Department of Chemistry

(4,5-c)Furotropyliene has the required structure and the required number of pi-electrons to belong to the class of aromatic carbenes, a group of carbenes that show predominantly singlet behavior and react preferentially with electron-poor olefins. Contrary to this expectation, (4,5-c)furotropyliene appears to behave as a triplet above about 40° C. and adds to ordinary olefins. It also has the unusual property of undergoing the first step of carbene-carbene rearrangement at low temperatures. The second step of rearrangement, opening of the intermediate cyclopropene to the rearranged carbene, is not detected. Possible rearrangement, though not disproved, is shown not to be the predominant reaction path such as is seen in certain slightly destabilized aromatic carbenes.

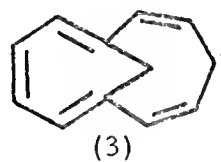
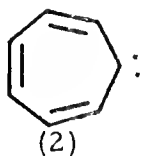
INTRODUCTION

It has been established that incorporating a vacant orbital of a carbene into a ring containing conjugated double bonds can, when the resulting system obeys the Huckel " $4n + 2$ " rule, result in establishment of so-called "aromatic" carbene systems that have unusual reactivity patterns.^{1, 2, 3, 4} These conditions are satisfied when the number of double bonds conjugated with the vacant orbital of the carbene is an odd number. (See Figure 1.)



(Figure 1)

Examples of such aromatic carbenes include the 2- π -electron system diphenylcyclopropenylidene (1),⁴ the 6- π -electron system, cycloheptatrienylidene (2),^{1, 2} and the 10- π -electron carbene derived from the 1,6-methano(11) annulene ring system (3).⁵ (See Figure 2.)



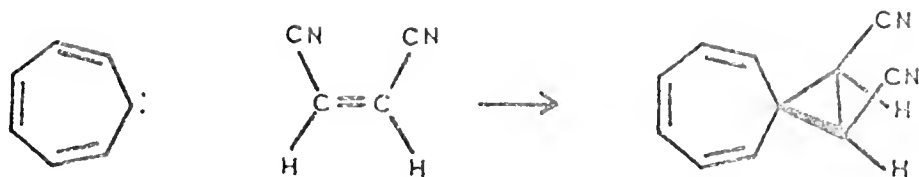
(Figure 2)

Aromatic carbenes display behavior patterns that are significantly different from those shown by other carbenes. The delocalization of charge density from the conjugated double bond system into the vacant orbital of an aromatic carbene can be expected to increase the nucleophilicity of the carbene. Also the carbene orbitals can be expected to split into two different energy levels, affording the possibility of a stabilized singlet state. (See Figure 3.)



(Figure 3)

Perhaps the most well known of these aromatic carbenes is cycloheptatrienylidene (2).^{1, 2} This carbene shows the properties one might expect of a stabilized singlet with increased nucleophilic character. It prefers to react with electron-deficient, rather than electron-rich, olefins. For example, in a Hammett study with substituted styrenes, cycloheptatrienylidene showed a reaction rate constant of +1.05.⁶ This compares with reaction rate constants of -0.619 for dichlorocarbene and -0.38 for carbethoxycarbene.^{7, 8} Not only is the sign of the reaction rate constant significant, but there is also significance in its larger absolute value, an indication that cycloheptatrienylidene is more discriminating than other carbenes; i. e., more stable. Consistent with the hypothesized stabilization of its singlet state, cycloheptatrienylidene reacts with acceptor olefins to form cyclopropanes in which the olefin stereochemistry is preserved.⁹ (Figure 4.)



(Figure 4)

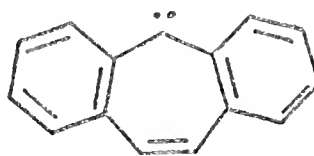
Among the substituted cycloheptatrienylenes that have been prepared and studied, the following annelated compounds have shown some interesting new departures in cycloheptatrienylidene chemistry. (Figure 5.)

Carbenes (4) and (5) have been generated under conditions that allow observation of their low-temperature esr spectra. Both have triplet ground states and react with electron-rich olefins such as 2-butene to form cyclopropane adducts.^{10, 11, 12} Evidently both (4) and (5) behave much like diphenylcarbene. Annelation has, in these two cases, changed the cycloheptatrienylidene so significantly that a singlet ground state is impossible. Carbenes (6), (7), and (8) show even more dramatic effects of annelation upon cycloheptatrienylidene. All three of these undergo carbene-carbene rearrangement at low to moderate temperatures according to the following equations.^{13, 14, 15} (Figure 6.)

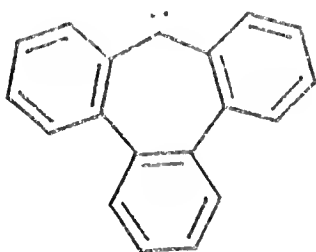
The ground states for these carbenes are unknown, but it is assumed that the rearrangements, at least, proceed through a singlet state.^{16, 17} The nature of the intermediate or transition state leading to this kind of carbene-carbene rearrangement has been somewhat controversial. There is recent convincing evidence that such rearrangements proceed via a cyclopropene intermediate such as shown



(2)



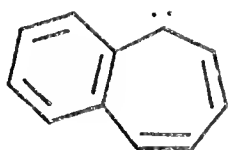
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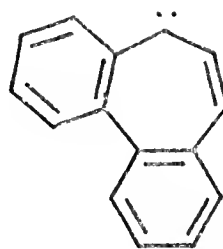
(5)



(6)

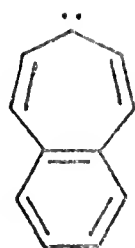


(7)

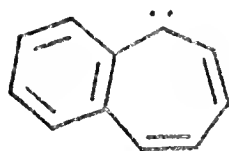
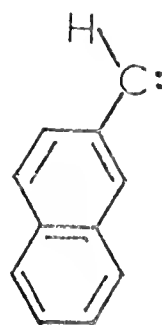


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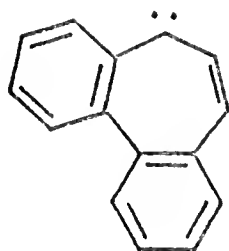
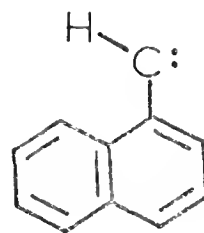
(Figure 5)



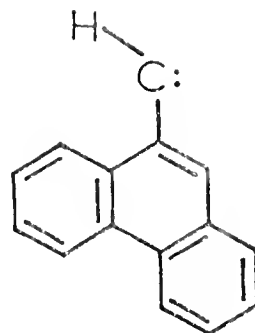
(6)



(7)

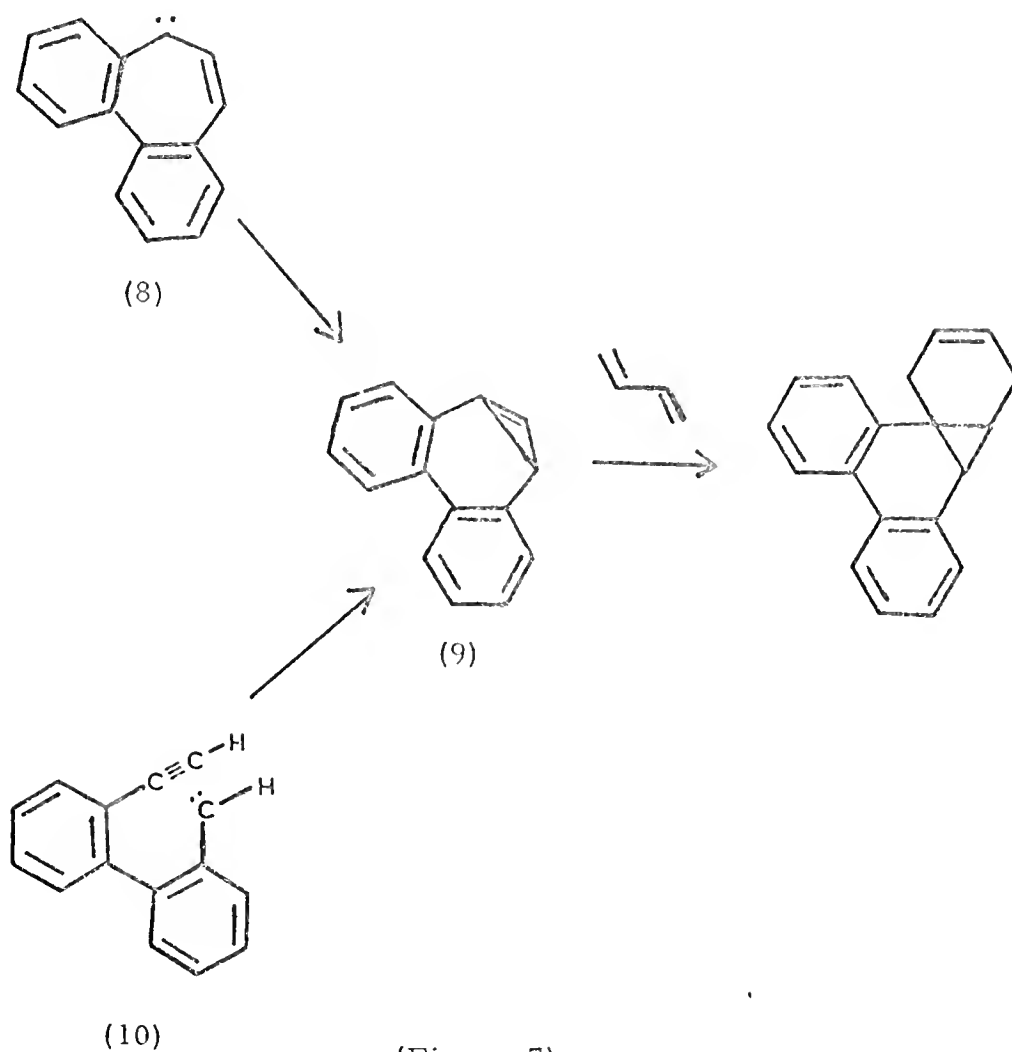


(8)



(Figure 6)

in Figure 7.¹⁵ In this example, the intermediate cyclopropene (9) appears to have been trapped by a Diels-Alder reaction with each of several dienes. The intermediate (9) has also been approached from another source as shown in Figure 7.¹⁸

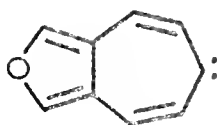


(Figure 7)

Monoannellation is said to substantially decrease the stability of the tropylium cation.¹⁹ Since carbene stability is thought to parallel cation stability, and since monoannellation should have little effect upon the stability of the intermediate cyclopropene, monoannellation is

thought to cause a destabilization of the carbene relative to the cyclopropene intermediate, thus increasing the probability of rearrangement.²⁰ Following this line of reasoning further, one could expect to anticipate rearrangements in other carbenes by an analysis of aromaticity and cation stability relative to the tropylium system.

The subject of this study is the carbene (4,5-c)furotropyliene (11) shown in Figure 8. This carbene should be expected to show at least some aromatic character, since it does satisfy the Huckel $4n + 2$



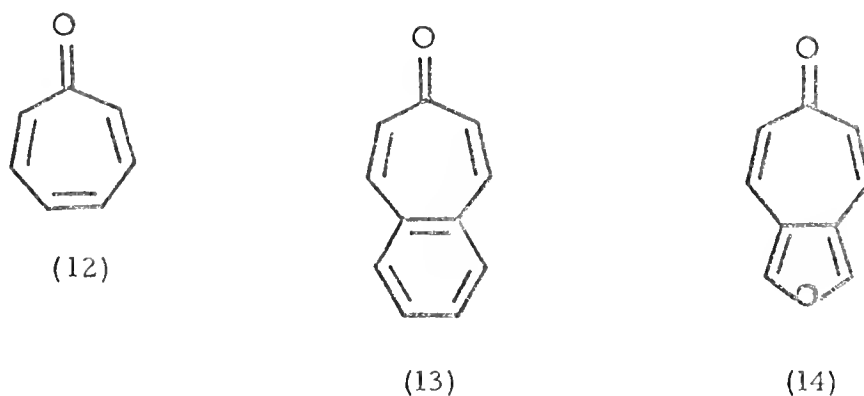
(11)

(Figure 8)

rule ($n = 2$), having 10 pi-electrons. The structure is not actually a simple annelated cycloheptatrienyliene in one sense, because it lacks a double bond analogous to the one between positions 4 and 5 in cycloheptatrienyliene.

The question of whether aromatic character can be expected in carbene (11) cannot be answered a priori. In fact, the whole concept of aromaticity in troponoid ketones has been attacked by Bertelli;^{21,22} but the concept seems so useful in explaining the behavior of troponoid-derived carbenes that its continued use seems justified for the time being. The following analysis, though it is mitigated by Bertelli's argument, has been used to arrive at estimates of relative aromaticities in the following series of ketones.²³

As delocalization of electrons increases in the ring systems, the bond order of the exocyclic $C=O$ groups will decrease. This will

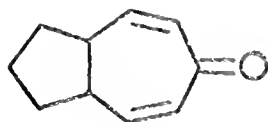


(Figure 9)

parallel the increasing contribution of the dipolar form of the carbonyl group $\overset{+}{\text{C}}-\overset{-}{\text{O}}$, thus paralleling the ability of the ring system to stabilize positive charge at the carbonyl carbon atom. This trend should be in the same direction as cation stability, thus in the same direction as carbene stability.

A measure of C=O bond order can be obtained by a study of the carbonyl absorption positions in the infrared spectra of the ketones in this series. It has been shown that, for geometrically similarly disposed C=O groups, there is good correlation between the frequency of absorption and the calculated bond order; i. e., as bond order of the carbonyl group increases, the higher will be the absorption frequency. As the aromaticity in the series of ketones increases, the bond order of the C=O groups should decrease, showing a lower infrared absorption frequency. The ketone (4,5-c)furotropone (14), having a C=O absorption at 1599 cm.^{-1} is therefore less aromatic than benzotropone (13), having its C=O absorption at 1590 cm.^{-1} . In turn, benzotropone (13) is less aromatic than tropone, since the carbonyl frequency of

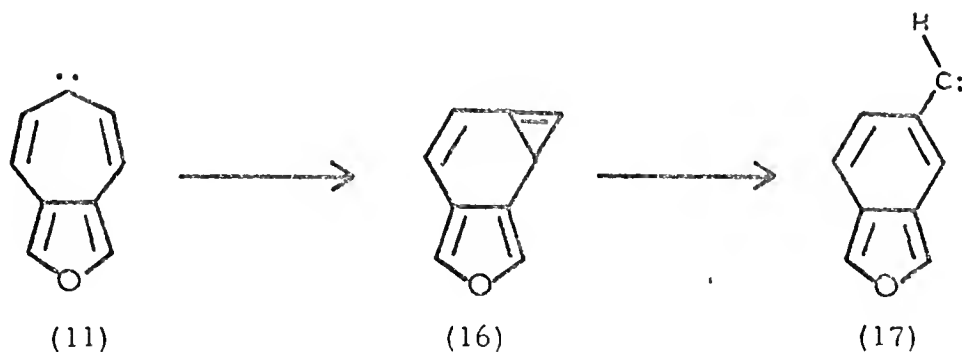
tropone (12) is 1582 cm.^{-1} . By this criterion furotropone (14) has more delocalization than a cross-conjugated cycloheptadienone because all its bands appear at lower frequencies than the carbonyl band of the dienone (15) shown in Figure 10 (ca. 1635 cm.^{-1}).²³



(15)

(Figure 10)

The inference that furotropyliene (11) should have less aromatic character than cycloheptatrienylidene (2) suggests that furotropyliene, like other slightly destabilized aromatic carbenes (6), (7), and (8), might be expected to undergo carbene-carbene rearrangement. The examination of a hypothetical reaction pathway of a hypothetical reaction pathway (Figure 11) suggests a possible complication. Although the carbene (11) should be destabilized relative to the



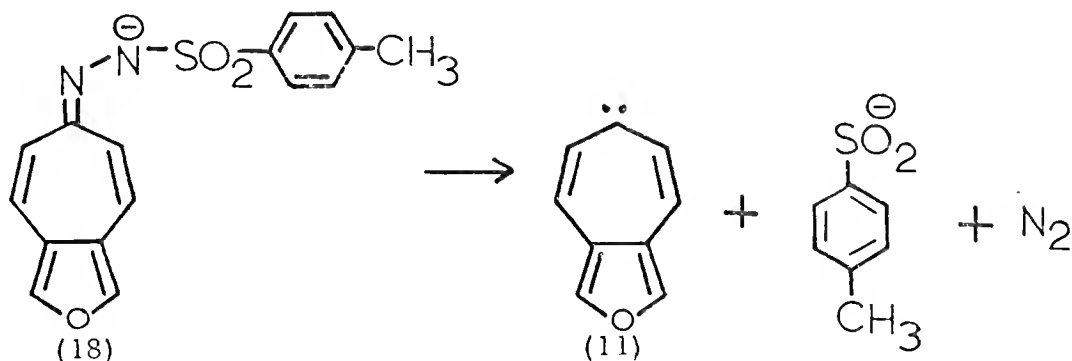
(Figure 11)

cyclopropene (16), the product (17) from opening the cyclopropene should give some caution. The rearranged carbene (17) has a carbene center attached to an isobenzofuran skeleton. Although isobenzofuran is a 10- π system, it apparently does not show the stabilization

associated with other aromatic systems. The parent hydrocarbon, isobenzofuran, has been prepared for the first time only recently.²⁴ It polymerizes readily in solution at moderate temperatures. The reaction pathway in Figure 11 suggests that, for the first time, one of the destabilized, partially aromatic carbenes might be headed into a rearrangement pathway in which product stability is quite low. This is in contrast to the highly stabilized aromatic products of carbene rearrangements presented on page 4. The effect of this point will become apparent as the results of this study are presented.

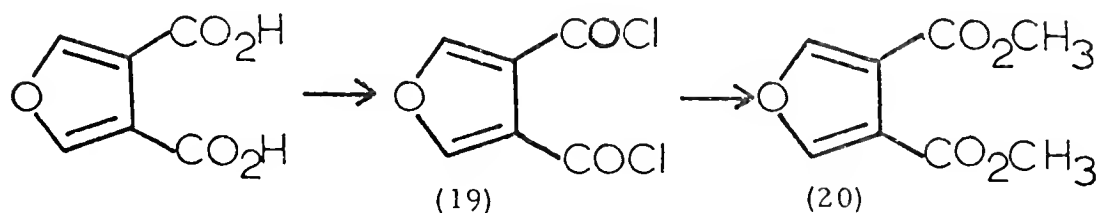
RESULTS

The carbene (4,5-c)furotropolidene (11) was prepared in all cases either by pyrolysis or photolysis of the sodium salt of the tosylhydrazone of (4,5-c)furotropone (18). The synthetic scheme for



(Figure 12)

producing the required ketone was originally developed by Cook and Forbes.²³ Some modifications of their procedures were used in preparing the ketone for this study. For example, commercially available furan-3,4-dicarboxylic acid was converted to its diacyl



(Figure 13)

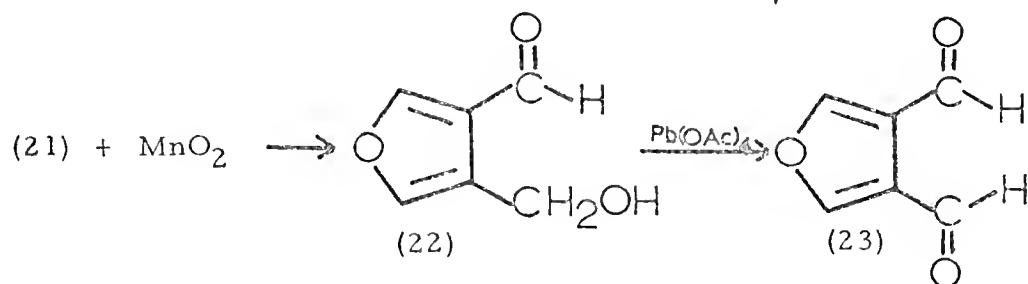
chloride (19) by the action of thionyl chloride in the presence of a catalytic amount of N,N-dimethylformamide. The acid chloride (19) was never purified and characterized. Its presence was inferred from

its reaction with methanol to afford a quantitative yield of the known dimethyl ester (20), previously characterized and reported by Cook and Forbes.²³ Using the procedures of Cook and Forbes, the reduction of the dimethyl ester was carried out using lithium aluminum hydride, but the 76 percent yields reportedly attainable did not result. Direct reduction of the crude diacyl chloride (19) did afford the di-alcohol (21) in yields of about 70 percent. The di-alcohol was treated



(Figure 14)

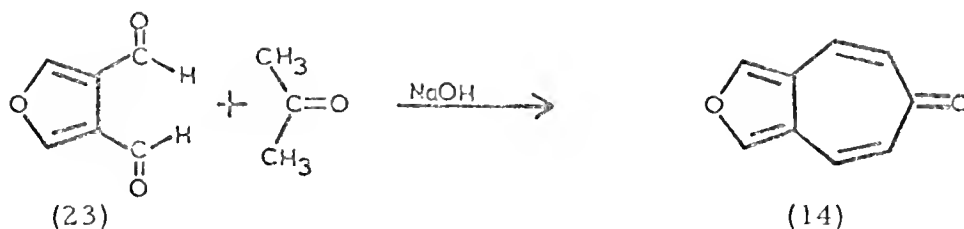
with activated manganese dioxide to effect oxidation of one of the alcohol groups to the aldehyde stage. Again the yields reported in the literature did not result.²³ The reaction usually produced only about 50 percent of the maximum amount of 3-hydroxymethyl-furan-4-carboxaldehyde (22), accompanied by about half of the unreacted di-alcohol (determined by proton resonance spectroscopy). This situation was made usable by the fact that lead tetra-acetate oxidation of this crude mixture of di-alcohol and mono-aldehyde afforded the



(Figure 15)

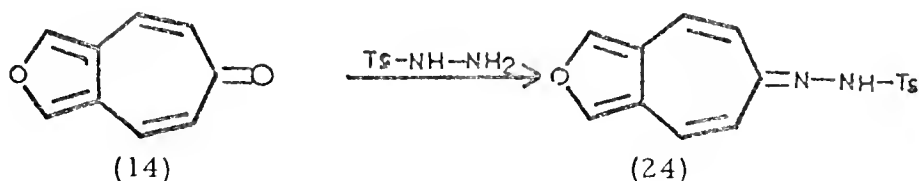
di-aldehyde (23) in yields of about 24 percent based on di-alcohol.

The 3,4-furandicarboxaldehyde (23) was condensed with acetone using the procedure of Cook and Forbes to give exactly the reported yield of 38 percent.²³



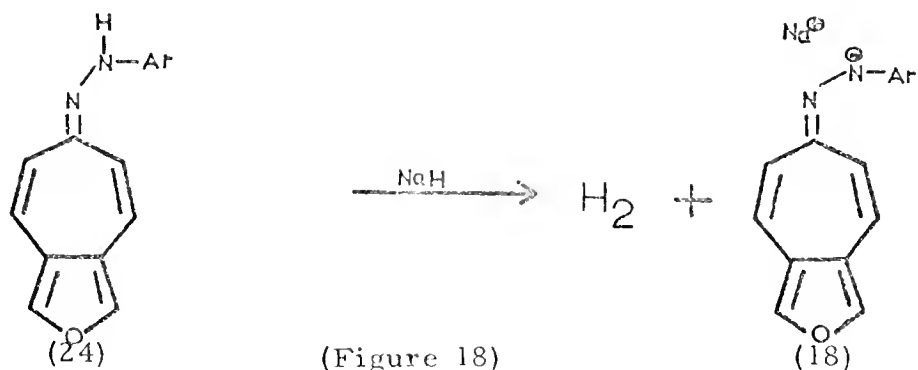
(Figure 16)

Conversion of furotropone into its tosylhydrazone was best carried out by treatment of the ketone (14) with tosylhydrazine in tetrahydrofuran containing a trace of anhydrous phosphoric acid. The reaction worked best when the reactants were merely allowed to stand together at room temperature for five to seven days. This procedure gave the tosylhydrazone (24) in 65-70 percent conversion.

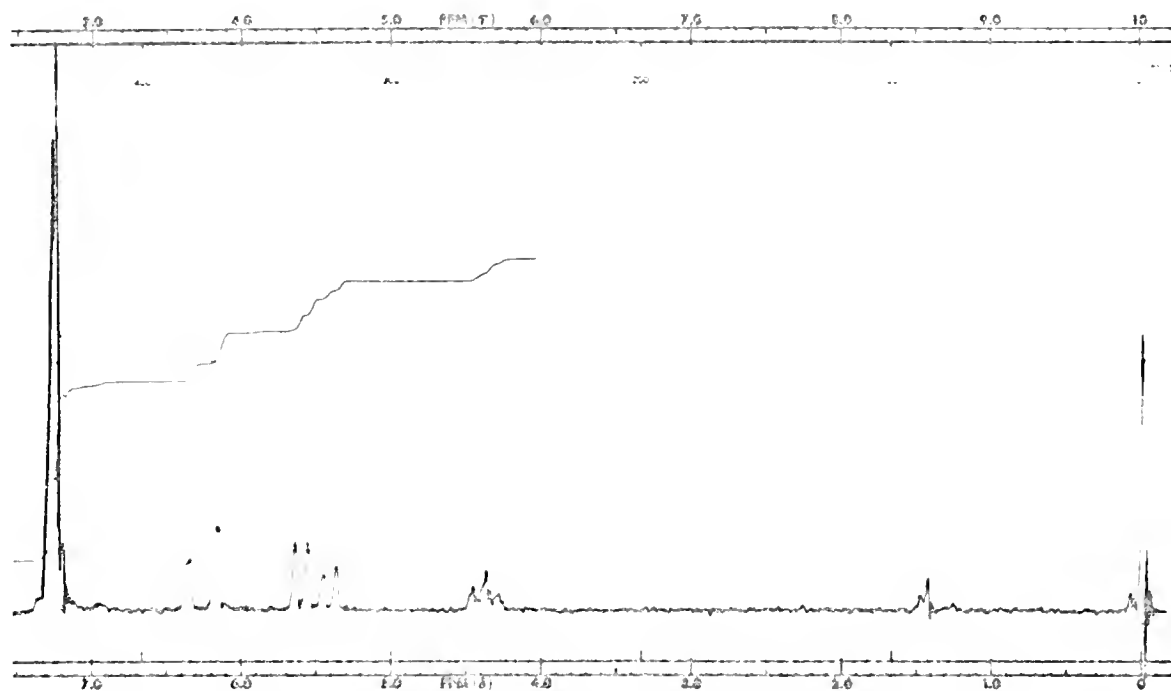


(Figure 17)

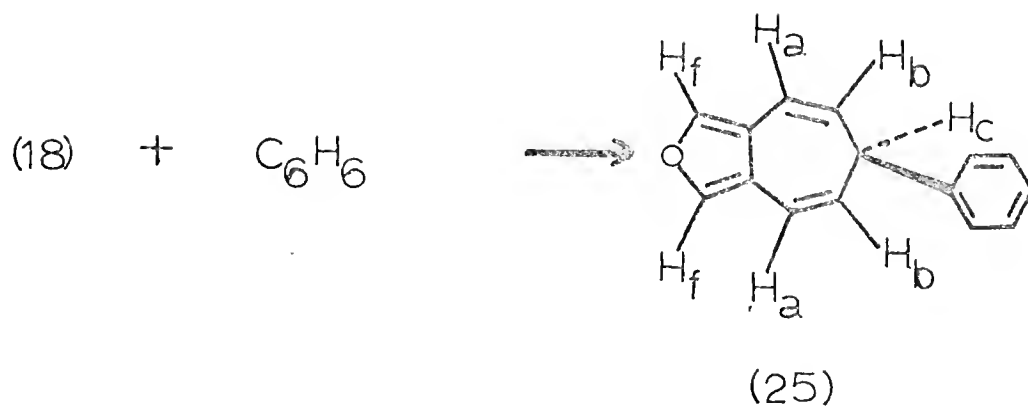
A solution of the tosylhydrazone in tetrahydrofuran was treated with sodium hydride to produce the sodium salt of the tosylhydrazone (18). The weight of the sodium salt produced suggests from the stoichiometry of the reaction that one mole of tetrahydrofuran is included in the salt as bound solvent. All yields in reactions of this sodium salt have been adjusted to reflect this effect.



Thermal decomposition of the sodium salt of (4,5-c)furotropone tosylhydrazone (18) in the presence of benzene at 188° C. led to formation of the formal C-H insertion product (25) in 43 percent isolated yield. The structure of (25) was assigned primarily on the basis of its spectral properties. At tau 2.71 and 2.72 there were two singlets, assigned to the furan hydrogens and to the benzene hydrogens, respectively. The total of both peaks was seven hydrogens. The vinyl hydrogens (H_a) appeared at 3.5-3.9 tau as a doublet, split by 11.5 Hz. through coupling to (H_b). Each peak of this doublet showed a slight splitting (ca. 1 Hz.) attributable to allylic coupling to the tertiary hydrogen (H_c). The vinyl hydrogens (H_b) appeared as a doublet of doublets at tau 4.33-4.6. In this pattern the coupling (11.5 Hz.) between vinylic protons and the coupling (5-5.3 Hz.) between (H_b) and (H_c) were both easily discernible. The tertiary hydrogen (H_c) appeared at tau 5.64. It was primarily a triplet pattern showing some superimposed allylic splitting. The infrared spectrum indicated the monosubstituted benzene structure by its absorptions at 762 cm.⁻¹ and 700 cm.⁻¹



PROTON MAGNETIC RESONANCE SPECTRUM OF PRODUCT
(25)



(Figure 19)

The proton magnetic resonance spectrum of the crude reaction mixture showed only the benzene C-H insertion product (25). No evidence of a cycloheptatriene structure was present. Careful examination of the reaction mixture by analytical thin-layer chromatography failed to show any biphenyl in the sample.

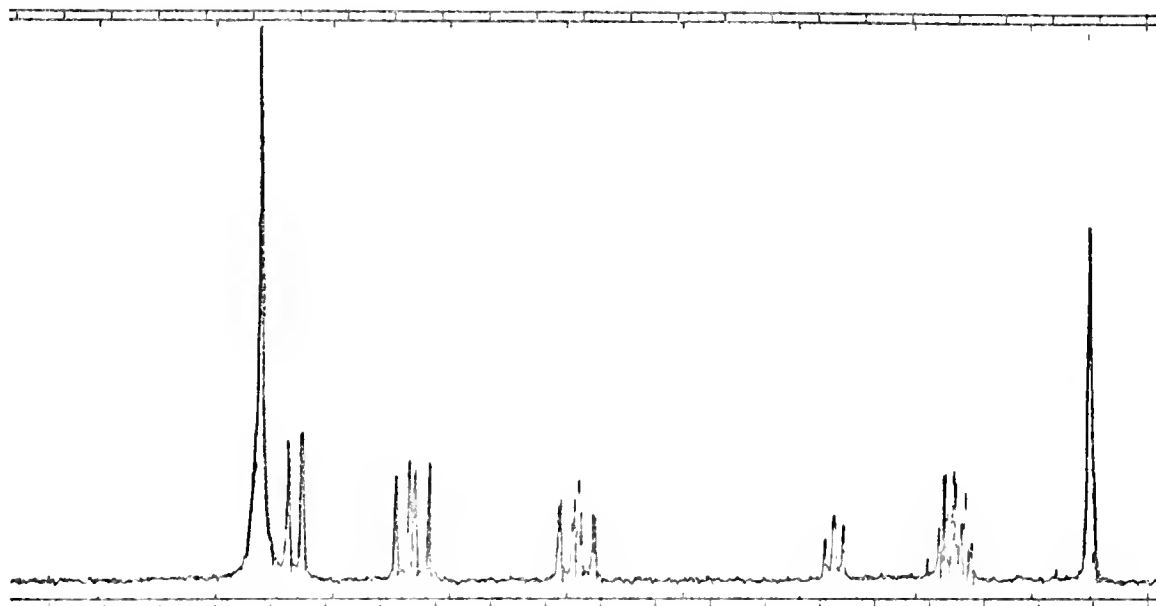
In a competition reaction allowing the carbene equal access to benzene and d_6 -benzene, essentially equal amounts of deuterated and non-deuterated products were produced as determined by both mass spectroscopy and by 100 MHz. proton magnetic resonance.

An effort to prepare the product of C-H insertion into cyclohexane failed because of low yields. The carbene (11) undergoes reaction with olefins in dioxane solution without taking dioxane into the reaction mixture. These observations suggest that the benzene C-H insertion reaction probably does not result from direct insertion, but through an intermediate that will be discussed in a later section of this report.

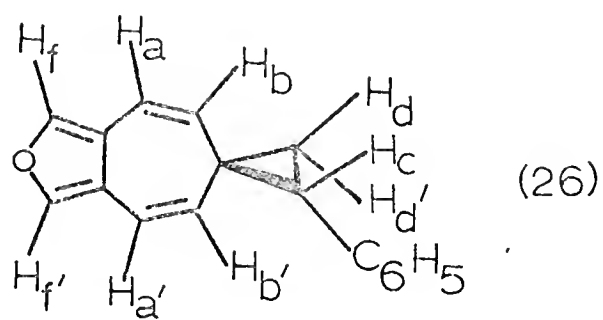
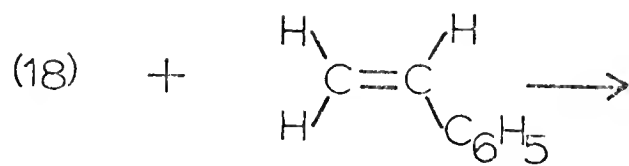
Attempted addition of the carbene (11) to the double bond in cyclohexene resulted in a mixture that could not be separated cleanly enough to allow characterization of any of the products. The proton magnetic resonance spectrum of the crude product did suggest that some addition to the double bond had occurred. The presence of other products in the reaction mixture suggests that (4,5-c)furotropyliene is not incapable of C-H insertion, but one is left to speculate about whether the products arise by direct reaction of the carbene or by secondary processes.

Decomposition of the tosylhydrazone salt in a refluxing solution of styrene in dioxane (b. p. $101^{\circ}\text{C}.$) was successful in producing a

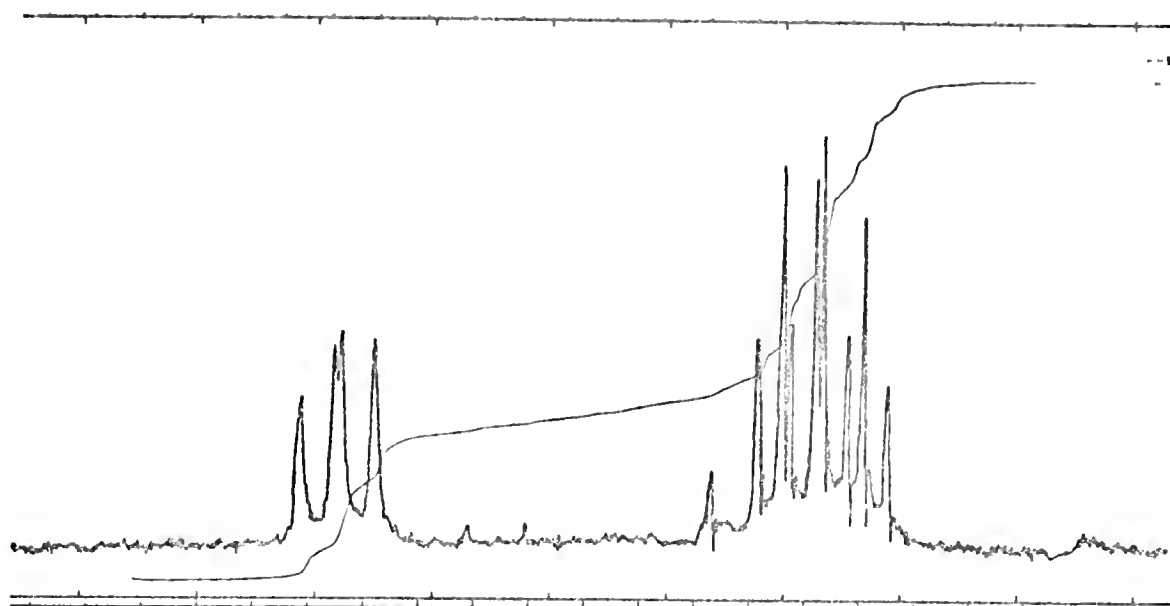
phenylcyclopropane (26) that could be separated and characterized. Yields as high as 50 percent were produced in solutions that were quite dilute (1.5-3 percent styrene). Little, if any, dioxane was attacked by the carbene. The major side-reaction was production of considerable amounts of polystyrene. The 100 MHz. magnetic resonance spectrum of the phenylcyclopropane (26) showed a sharp singlet at τ 2.86 with a correct integral for the five phenyl hydrogens. There were two small singlets (total 2H for both) representing the furan hydrogens, nonequivalent in this molecule, at τ 2.96 and 3.01. The vinylic hydrogens (H_a) and ($H_{a'}$) appeared as two doublets in the region from 4.0 to 4.33 τ . Each of the doublets was split by 12 Hz. through coupling to the hydrogens (H_b) and ($H_{b'}$). The value of this coupling between cis olefinic hydrogens suggests that they are connected to a seven-membered ring.²⁵ The hydrogens (H_b) and ($H_{b'}$) appear as two doublets at 5.25 to 5.95 τ , again spaced by about 12 Hz.; but each peak in these doublets is split very slightly again (about 2 Hz.), suggesting coupling across the ring between (H_b) and ($H_{b'}$). This coupling is to be expected because these hydrogens (non-equivalent because of the phenyl group) are situated for W-form coupling. Although the furan hydrogens are also situated for W-form coupling, and their chemical shift difference is ca. 12 Hz., the coupling between them is only barely discernible. It is interesting to note that the facing pairs of hydrogens on the seven-membered ring and in the furan system show decreasing chemical shift differences with increasing distance from the symmetry-disturbing phenyl group. The cyclopropyl hydrogens in the phenylcyclopropane (26) present the expected ABX pattern. The (H_c) hydrogen (X) appears in the 7.53-7.85



PROTON MAGNETIC RESONANCE SPECTRUM OF PRODUCT
(26)

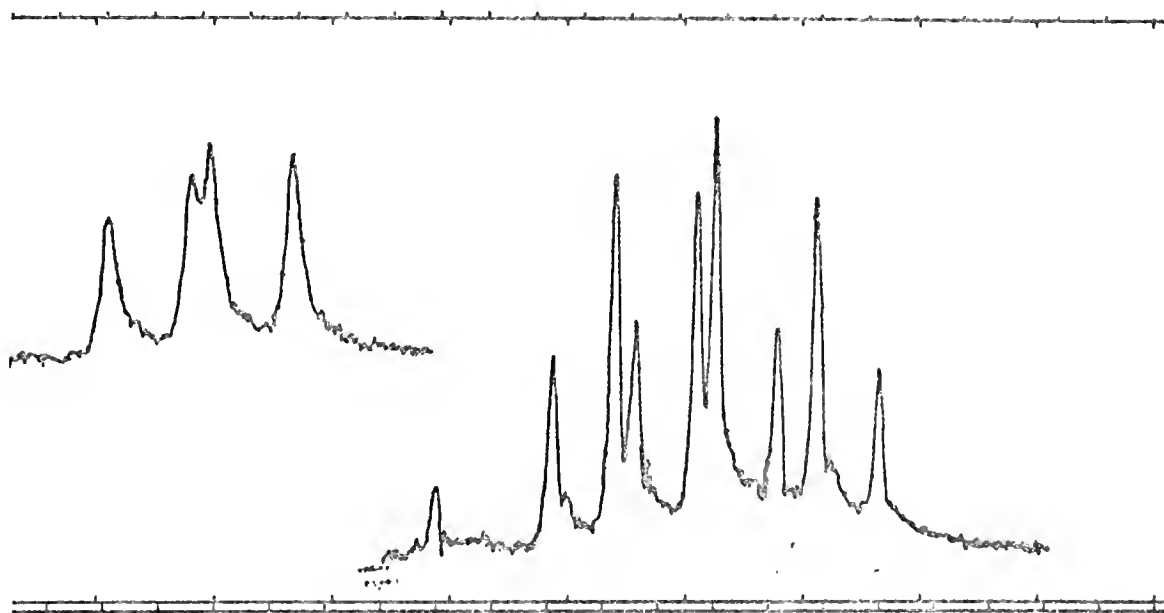


(Figure 20)



PROTON MAGNETIC RESONANCE SPECTRUM OF PRODUCT
(26)

ENLARGED VIEWS OF ABX PORTION

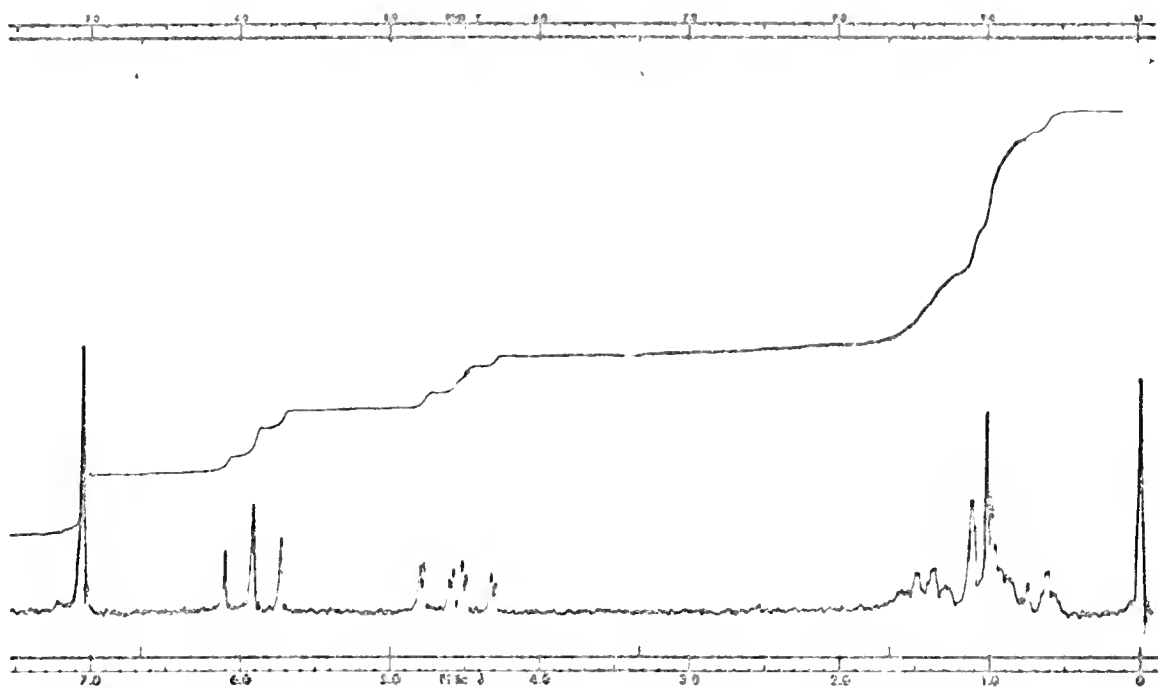


(Figure 21)

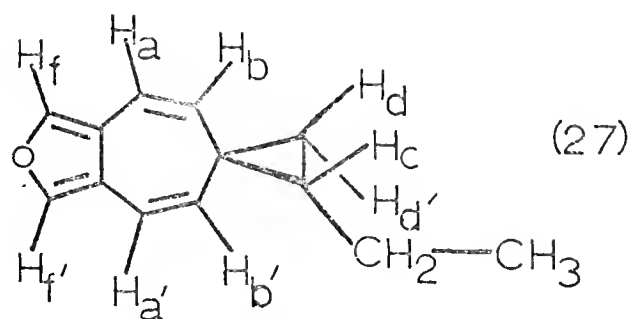
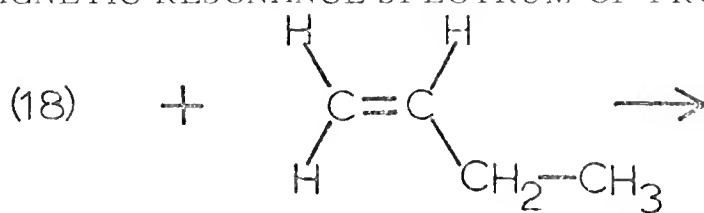
tau area as two doublets that show overlap between the two central peaks. The geminal cyclopropyl hydrogens (AB pair) appear as the expected pair of overlapping quartets in the region 8.7-9.0 tau. The spacing between the midpoints of the two quartets ($1/2$ abs. value of $J_{AX} + J_{BX}$) allows easy calculation of the predicted spacing between lines 9 and 12 in the X portion of the spectrum. The predicted spacing between lines 9 and 12 (15.6 Hz.) was observed and permitted assignment of lines 9 and 12 as the two outside lines in the X portion of the spectrum.²⁶ The value of $J_{AB} = 5.4$ Hz. was directly measurable from the spectrum.

The infrared spectrum of (26) shows absorptions near 700 cm.^{-1} and 750 cm.^{-1} , consistent with the mono-substituted benzene structure. Absorptions at 860 cm.^{-1} and 1028 cm.^{-1} offer confirmatory evidence of the cyclopropane ring indicated by the absorption at 3060 cm.^{-1} .²⁷

Pyrolytic decomposition of the tosylhydrazone salt (17) in the presence of 1-butene gave the expected ethylcyclopropane (27) in about 50 percent isolated yield. The cyclopropane was accompanied by three minor by-products that were never identified. The proton magnetic resonance spectrum of (27) showed a two-hydrogen singlet at 2.95 tau for the furan hydrogens. The vinylic protons (H_a) and ($H_{a'}$) that showed a pair of doublets in the phenylcyclopropane (26) appeared in this ethylcyclopropane as an overlapped pair of doublets split by 11.5 Hz. at tau 3.87-4.3. The other pair of vinylic hydrogens (H_b) and ($H_{b'}$) appeared as a pair of separated doublets at 5.25-5.8 tau showing the same W-form coupling observed in the phenylcyclopropane (26). It is interesting to observe the smaller symmetry disturbance



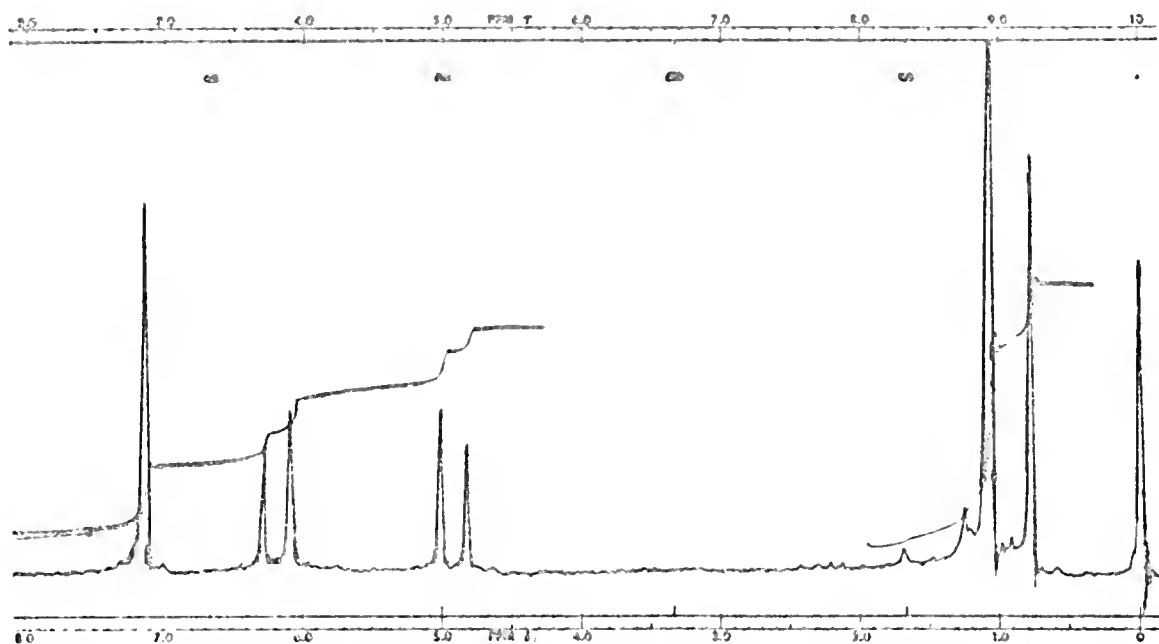
PROTON MAGNETIC RESONANCE SPECTRUM OF PRODUCT (27)



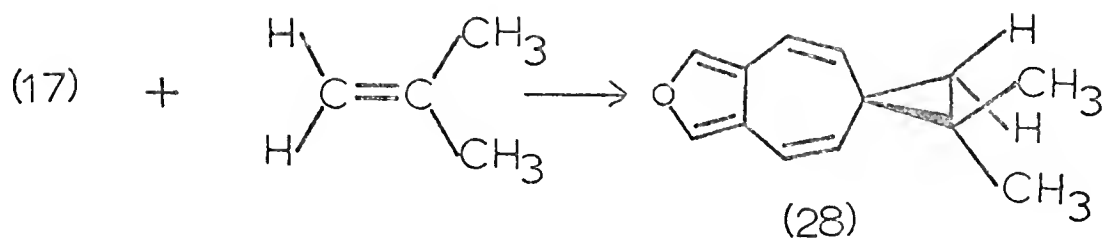
(Figure 22)

produced by the ethyl group in (27) compared with the larger effect of the phenyl group in (26). Whereas the furan hydrogens were resolvable in (26), they were not resolvable in (27). Further evidence of lower disturbance of symmetry is provided by the fact that the pair of doublets representing the vinylic hydrogens (H_a) and ($H_{a'}$) are overlapped in (27), but well separated in (26). The remainder of the spectrum of the ethylcyclopropane (27) was a complex eight-hydrogen signal in the region of 8.3-9.5 tau that included the cyclopropyl hydrogens and the hydrogens on the ethyl group.

Thermal decomposition of the tosylhydrazone salt (17) in the presence of isobutene gave a remarkably clean reaction producing the dimethylcyclopropane (28) in 28 percent yield. The structure was assigned primarily on the basis of the proton magnetic resonance spectrum. This molecule provides an excellent example of the profound effects of molecular symmetry on nuclear magnetic resonance. A plane of symmetry can be drawn through the dimethylcyclopropane (28). This plane includes the plane of the cyclopropyl ring and bisects the plane of the fused furotropylium ring system. This symmetry results in magnetic equivalence of the furan hydrogens and both sets of vinyl hydrogens in the seven-membered ring. This results in a simplified spectrum for the compound. A two-hydrogen singlet for the furan hydrogens appeared at 2.83 tau. Instead of the more complex vinyl absorptions observed in the styrene adduct (26) and in the 1-butene adduct (27) a simple AB pattern appeared. A doublet centered at 3.81 tau showed a two-hydrogen signal for the (H_a) pair. Another doublet centered at 5.09 tau was presented by the (H_b) pair of hydrogens. The coupling between (H_a) and (H_b) was 11.5 Hz., about the same value



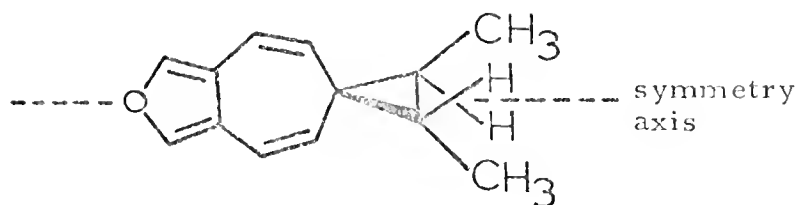
PROTON MAGNETIC RESONANCE SPECTRUM OF PRODUCT (28)



(Figure 23)

observed in other compounds in this series. The two methyl groups produced the expected six-hydrogen singlet at 8.9 tau, accompanied by a nearby singlet for the two equivalent cyclopropyl hydrogens at 9.2 tau.

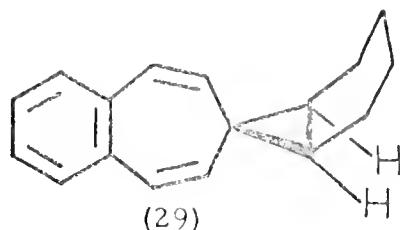
The profound effects of changes in symmetry in spirocyclopropanes such as (26), (27), and (28) provide an excellent basis for assignment of stereochemical configurations in cis- and trans-1,2-disubstituted spirocyclopropanes by nuclear magnetic resonance. Trans-1,2-disubstituted spirocyclopropanes (see Figure 24) can be expected to have equivalent sets of furan hydrogens and vinylic hydrogens facing each other across the ring. This is because rotation



(Figure 24)

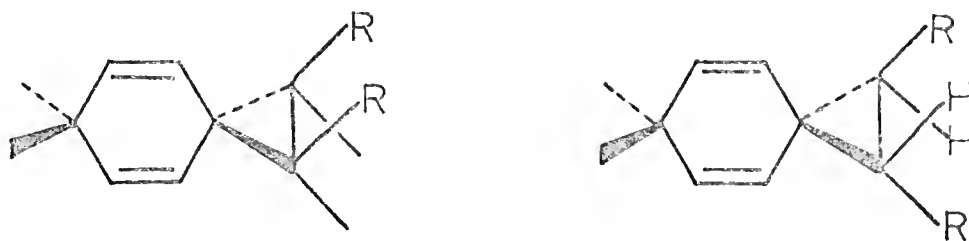
about the twofold axis of symmetry shown in the drawing makes these sets of hydrogens equivalent. On the other hand, cis-1,2-disubstituted spirocyclopropanes can be expected to show the same kind of complex pattern observed for the vinyl hydrogens as was seen in the monosubstituted spirocyclopropanes (26) and (27), resulting from the non-equivalency of facing pairs of hydrogens on the opposite sides of the seven-membered ring. A model for cis-disubstituted spirocyclopropanes of this type has been prepared by Krajca from the reaction of 4,5-benzotropyliene with cyclohexene.¹⁴ This compound (29) shows a nuclear magnetic resonance pattern in the vinyl region

that is essentially identical to the pattern shown by the phenylcyclopropane (26). A similar vinylic absorption pattern has been used to



(Figure 25)

assign stereochemical configurations in a series of spirocyclopropanes derived from the reactions of 4,4-dimethylcyclohexadienylidene with various olefins.²⁷ This is shown in Figure 26. Both cis- and trans-1,2-disubstituted spirocyclopropanes of this type were prepared.



(Figure 26)

Both isomers showed the expected effect of symmetry differences upon the nuclear magnetic resonance spectra in the vinylic region.

With the above-described basis for making stereochemical assignments in 1,2-disubstituted spirocyclopropanes, it is possible to study the stereospecificity of the reaction of furotropyliidene (11) with olefins. The stereospecificity test is widely used as a chemical test for distinguishing between singlet and triplet states in carbenes.^{28,29} Stereospecific addition; i. e., addition to olefins to produce cyclopro-

panes in which olefin stereochemistry is preserved, is characteristic of singlet carbenes. Non-stereospecific addition, in which olefin stereochemistry is not preserved, is characteristic of triplet carbenes.

A stereochemical study was undertaken using cis- and trans-2-butenes as acceptor olefins for the carbene (11). Thermal decomposition of the tosylhydrazone salt in the presence of cis-2-butene at 118-120°C. and in the presence of trans-2-butene at the same temperature produced two crude reaction mixtures that were virtually identical in their proton magnetic resonance spectra. Gas chromatographic examination of the crude reaction mixtures using a 100-foot capillary column coated with Ucon LB-550 showed at least 11 components in the reaction mixtures. Most of the chromatographic peaks were in the same quantitative relation to each other in both mixtures. Separation of the main peak on a preparative gas chromatographic instrument, though it gave a less-perfect separation than the capillary instrument, did allow some narrowing in the choice of the significant peaks in the chromatograms prepared on the capillary instrument, since this fraction was shown by nuclear magnetic resonance to contain the major components present in the crude product. The significant area turned out to be a group of two smaller peaks and one major peak that were not even well separated on the capillary instrument. Quantitative differences were seen in the relation of the two smaller peaks when comparing samples prepared by thermal reaction with the cis and trans olefins, but the significance of this difference between these two smaller peaks may be trivial because of the following observations: 1. The proton magnetic resonance spectra (vide infra) of

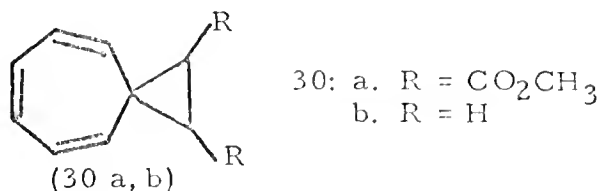
both reaction mixtures were identical. Both crude reaction mixtures appeared to be predominantly the trans-spirocyclopropane (vide infra).

2. There was no indication of the presence of the cis-spirocyclopropane in either sample to the limit of detection by the proton magnetic resonance spectra.

3. Thermal reaction of the tosylhydrazone salt with trans-2-butene is most likely to produce the more stable trans-spirocyclopropane if product isomerization is taking place. A photochemical decomposition of the salt in the presence of cis-2-butene is most likely to produce the cis-spirocyclopropane, because of expected lower probability of thermal cis-trans isomerization at the milder temperatures, ca. 50°C., used. A comparison of the capillary chromatograms of these two reactions showed the same quantitative relation among the three peaks in this significant area. Apparently the major peak is the trans-spirocyclopropane (vide infra). The two minor peaks were never identifiable for the reasons of small sample size and difficulty of purification. The proton magnetic resonance spectra suggest that these are probably mainly C-H insertion products. The attainment of the same product mixture from carbene reactions with a pair of isomeric cis-and trans-olefins is the criterion for complete loss of stereospecificity in the reaction.

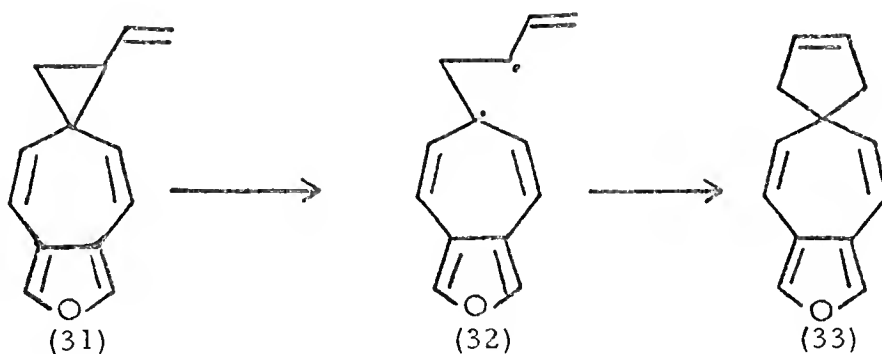
The failure to isolate any of the cis-spirocyclopropane from the reactions with the 2-butenes and to demonstrate the stability of the cis-isomer to reaction conditions does leave the experiment open to the criticism that the cis-isomer is possibly being formed, then is decomposing to either the trans-isomer or to some other product. This possibility is impossible to exclude rigorously in the present case, but some inferences for the stability of the cis-isomer can be drawn

from a study of known model compounds. Cyclopropanes of the type (30) are subject to a cleavage of the cyclopropyl ring followed by



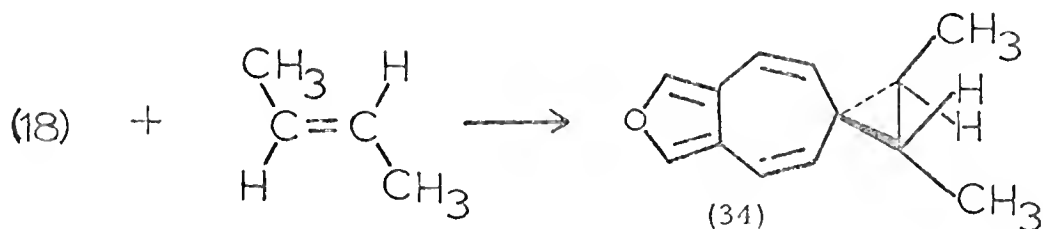
(Figure 27)

isomerization to an indane derivative. The substituted cyclopropane (30a) undergoes isomerization at 130°C ., but the unsubstituted cyclopropane (30b) is stable at 150°C . Similarly, one should expect an enhanced rate of isomerization in the vinyl-substituted spirocyclopropane (31) (Figure 28) because of stabilization of radical intermediate (32). The isomerization is slow at 100°C ., since the cyclopropane can be isolated as the main product from reaction mixtures exposed to that temperature for 0.5 hr. (vide infra). This suggests that cis-dialkyl-spirocyclopropanes would require substantially higher temperatures before isomerization to the trans isomer would occur at a significant rate.



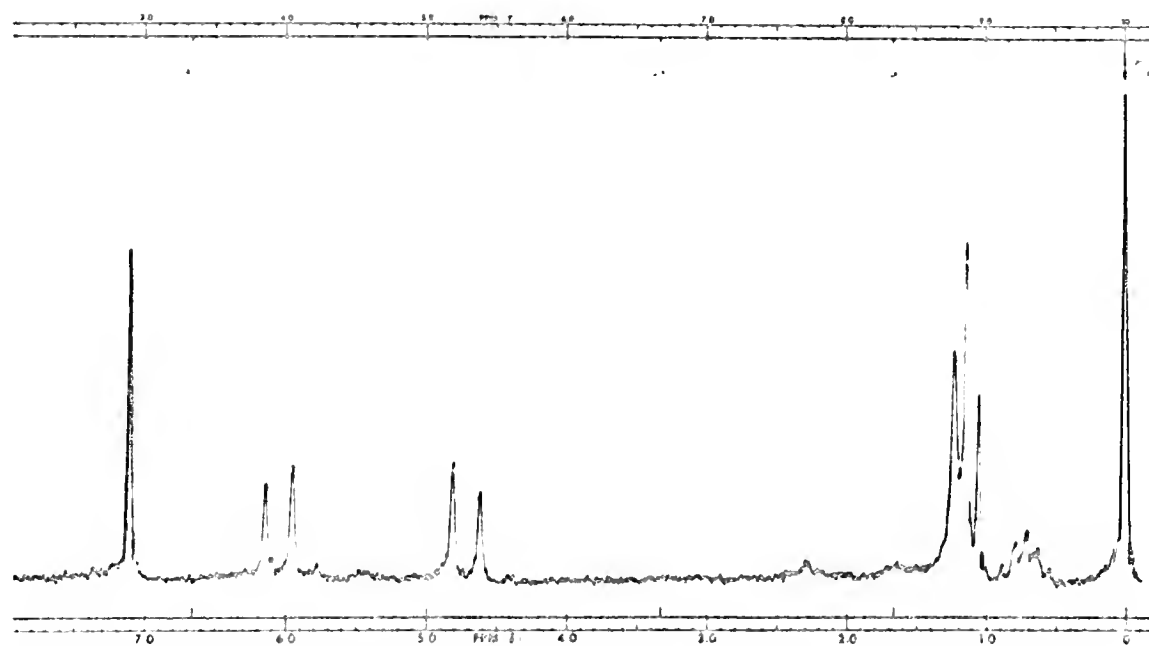
(Figure 28)

Isolation and characterization of the trans-spirocyclopropane produced from the reaction of carbene (11) with the cis- and trans-2-butenes proved to be as difficult as the foregoing discussion would suggest. Reaction of trans-2-butene by decomposition of the sodium salt at 115°C. produced a crude reaction mixture, the proton magnetic resonance spectrum of which suggested that the main component

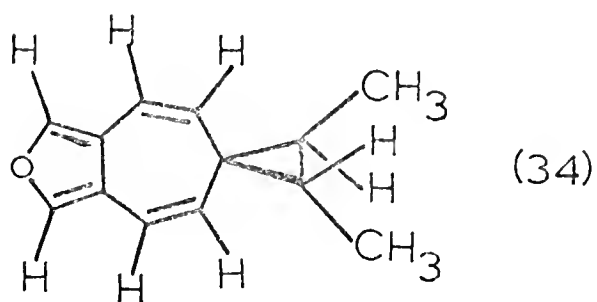
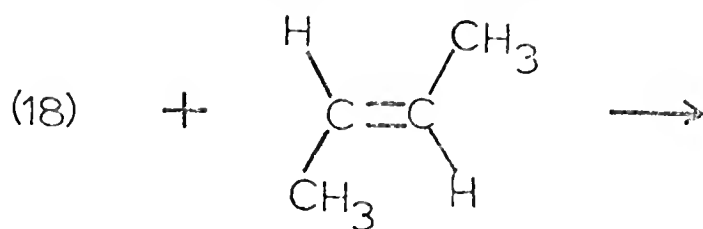


(Figure 29)

was the trans-1,2-dimethylcyclopropane (34) contaminated with C-H insertion products. Preparative layer chromatography on silica gel plates did not improve the appearance of the spectrum very much until the main band was collected and re-chromatographed on silica gel plates using very low sample loading. This allowed separation into three bands, the major one of which gave a spectrum suggesting a fairly pure sample of the trans-adduct (34). Because of small sample size, neither of the two minor components was identified. The yield of the trans adduct (34) appears to be in the neighborhood of 25 percent, but extensive handling of small samples makes this number unreliable. The assignment of the structure (34) rests primarily on the proton magnetic resonance spectrum. There is the usual sharp singlet at 2.9 tau for the furan hydrogens. From the discussion on pages 17, 18, and 19 one would expect the AB pattern that is observed in the vinylic region, produced by the hydrogens on



PROTON MAGNETIC RESONANCE SPECTRUM OF PRODUCT (34)



(Figure 30)

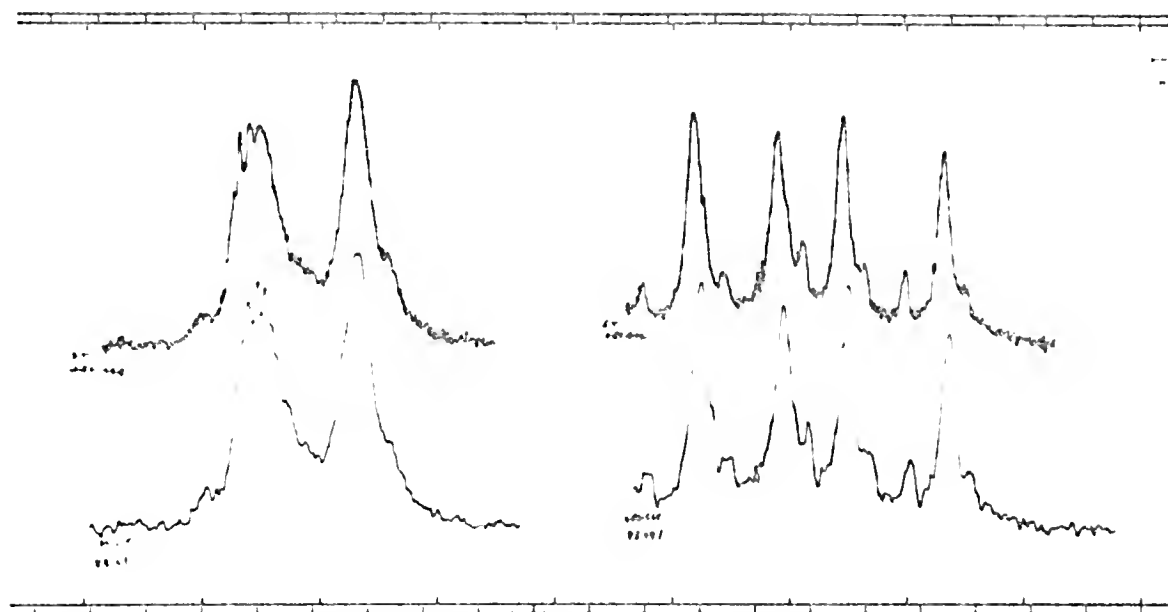
the seven-membered ring. One of the AB doublets is centered at 3.8 tau, the other at about 5.3 tau, with a coupling of 11.5 Hz. At 8.65 to 8.9 tau there are two peaks whose relative intensity suggests they are coupled to the cyclopropyl hydrogens that appear slightly upfield. There is a third sharp peak just downfield of these cyclopropyl hydrogens at about 8.93 tau, the shape and intensity of which leave its interpretation open to question. It is probably a spurious peak due to the presence of some impurity, but it could also be the result of so-called "virtual coupling" through the cyclopropyl hydrogens. The integration curve is not much help in deciding, since the effect of this peak on the total is not very great. The best integral does result from considering it to be a spurious peak, though. The spacing of this suspicious peak from the closest of the other two is, whether fortuitous or not, equal to the spacing between the other two and equal to one of the spacing patterns seen in the signal for the cyclopropyl hydrogens whose multiplet appears at 9.05 to 9.5 tau. The integration curve for the cyclopropyl hydrogens appears to fall just a little bit short of the required amount, but some of this signal may be buried under the "suspicious" peak already discussed. To judge from this spectrum, there is very little, if any, of the cis-spirocyclopropane present in the sample.

An overview of the results of the stereochemical study with the 2-butenes suggests that a study with another olefin, one that would hopefully give a cleaner reaction, would reinforce the argument for the loss of stereospecificity in addition reactions of this carbene. Accordingly a study was carried out using trans-deuteriostyrene as an acceptor for the carbene. From the experience gained with the non-

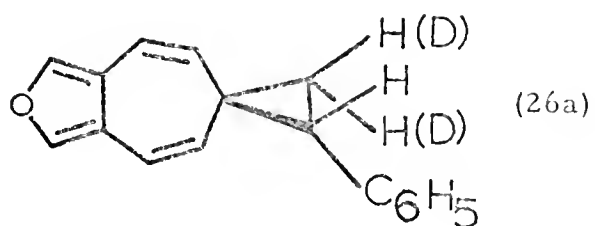
deuterated styrene reaction it was known that this reaction (shown in Figure 20) can be used to produce rather pure samples of the phenylcyclopropane.

The required deuterated styrene was prepared by the stereospecific addition of dicyclohexylborane to phenylacetylene followed by hydrolysis with deuterioacetic acid to free the styrene.³⁰ Formal addition of the carbene to this olefin was carried out by pyrolysis of the tosylhydrazone salt in a dilute solution of the olefin in boiling dioxane (b.p. 101° C.). The resulting phenylcyclopropane was separated by preparative layer chromatography. Use of d_6 -benzene as a solvent allowed observation of the geminal cyclopropyl hydrogens by 100 MHz. proton magnetic resonance spectroscopy as two doublets appearing at 8.7-9.2 tau. One of the doublets was split by 8.5 Hz.; the other, by 7.0 Hz. By double irradiation to decouple the neighboring cyclopropyl hydrogen (H_c) from the geminal pair, the four signals were caused to collapse to two signals having a separation of about 12 Hz. Integration of the four signals (before decoupling) and the two signals (after decoupling) showed the presence of an equal mixture of the two possible isomers.

Though the formation of an equal mixture of the two possible deuterio phenylcyclopropanes in this study suggests non-stereospecific addition of the carbene to the olefin, the result is not conclusive unless the possibility of olefin isomerization before reaction and the possibility of product isomerization after reaction are excluded. The olefin was determined to be stereochemically stable under the reaction conditions by a control experiment. The stability of the product is not so easily proved. Separation of the two stereoisomeric products is not



PROTON MAGNETIC RESONANCE SPECTRUM OF PRODUCT (26a)
SHOWING SIMPLIFICATION OF ABX



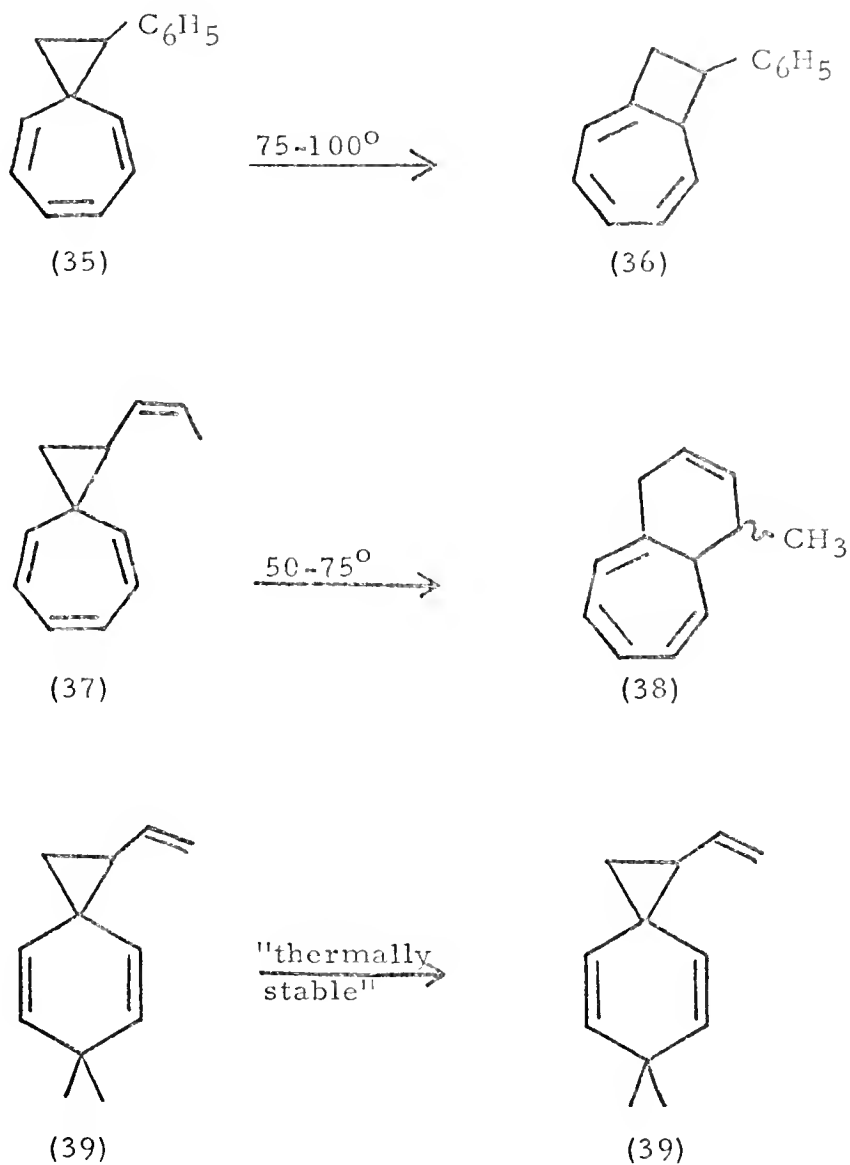
(Figure 31)

possible, so a direct test for isomerization under reaction conditions is not possible. The best remaining option is to conduct the reaction at a temperature at which product isomerization is highly unlikely. One can also draw inferences about the thermal stability and the photochemical stability of the phenylcyclopropane adduct by examination of model compounds (*vide infra*).

The reaction with *trans*-deuteriostyrene was repeated by decomposing the sodium salt of the tosylhydrazone photolytically at about 45°C. This procedure also produced an equal amount of the two possible stereoisomers. Though it might have been desirable to have carried out the photolysis at even lower temperatures, the properties of this carbene are such that it does not add readily to olefins at low temperatures. This point will be discussed further in connection with reactions of this carbene with butadiene. The styrene did not isomerize under photolysis.

The photolytic and thermal stability of the phenylcyclopropane (26a) can be inferred from the following data: 1. The vinylcyclopropane (31) (see Figure 28) requires temperatures greater than 100°C. for an appreciable rate of ring-opening, followed by closure to the cyclopentene (33). 2. The same vinylcyclopropane was determined (*vide infra*) to be photolytically stable under reaction conditions. 3. The somewhat similar 1-phenylspiro(2.6)nona-4,6,8-triene (35) shown in Figure 32 requires temperatures greater than 75°C. for isomerization to the 8-phenylbicyclo(5.2.0)nona-1,3,5-triene (36),³¹ but its isomerization is aided by the formation of a new stable compound of a type that cannot be formed from (26). 4. The vinylcyclopropane (37) rearranges to (38) at 50-75°C.³¹ On the other hand, the

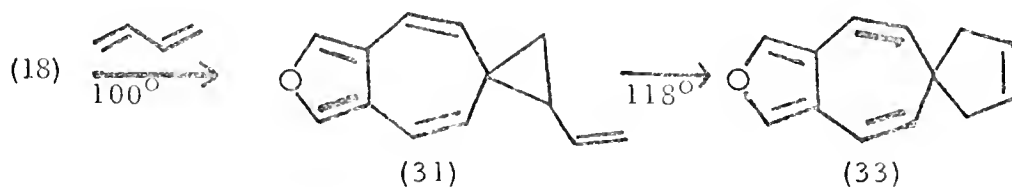
butadiene adduct (39) is stable enough to be isolated by preparative gas chromatography.²⁷



(Figure 32)

Pyrolysis of the tosylhydrazone salt (18) in the presence of 1,3-butadiene at $118^\circ C$. produces almost exclusively the 1,4-addition product (33) (55 percent yield) shown in Figure 33. It has been hypothesized that triplet carbenes might react with 1,3-dienes in the 1,4-addition mode. Few carbenes, if any, actually do add in this manner

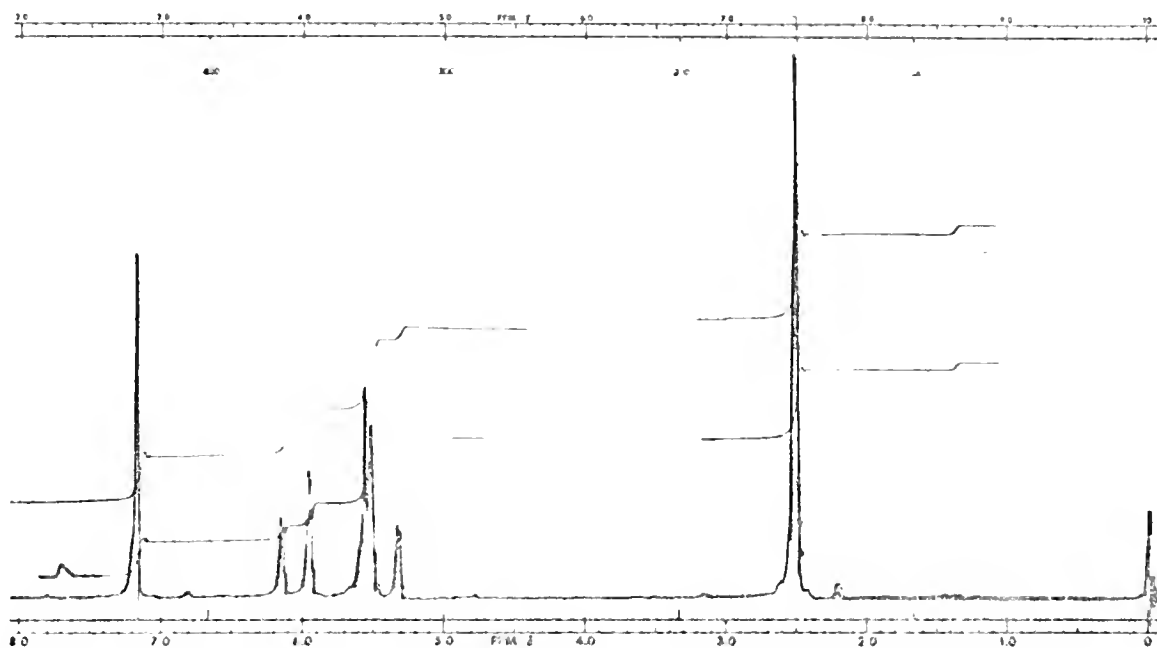
by direct reaction.³² Most adducts arising from a formal 1,4-addition are products from the thermal isomerization of initially formed 1,2-addition products such as (31). That proved to be true in this case also. Thermal decomposition of the tosylhydrazone salt in 1,3-butadiene at 100°C. for short reaction times (0.5 hr. or less) produced the 1,2 adduct (31). Heating of the vinylcyclopropane (31)



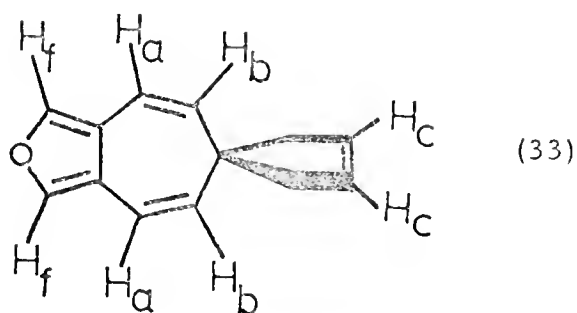
(Figure 33)

at 120°C. for 0.5 hr. caused complete conversion to the isomeric cyclopentene (33).

Structural assignment of the 1,4-addition product (33) was based on the following spectral data. In the proton magnetic resonance spectrum there is the expected two-hydrogen singlet at 2.82 tau for the furan hydrogens. Since this molecule has the same kind of symmetry as the dimethylcyclopropane (28) shown in Figure 22, one can predict the same kind of AB pattern for the vinyl hydrogens (H_a) and (H_b) in the seven-membered ring. This expected four-line AB pattern is observed in (33). One of the doublets in the AB pattern is centered at 3.9 tau and is split by 11.5-12 Hz. The other doublet is centered at 4.57 tau (representing the (H_b) hydrogens), but the left half of the doublet has a partially superimposed peak from the vinylic hydrogens in the cyclopentene ring (H_c). The integral for the lower-



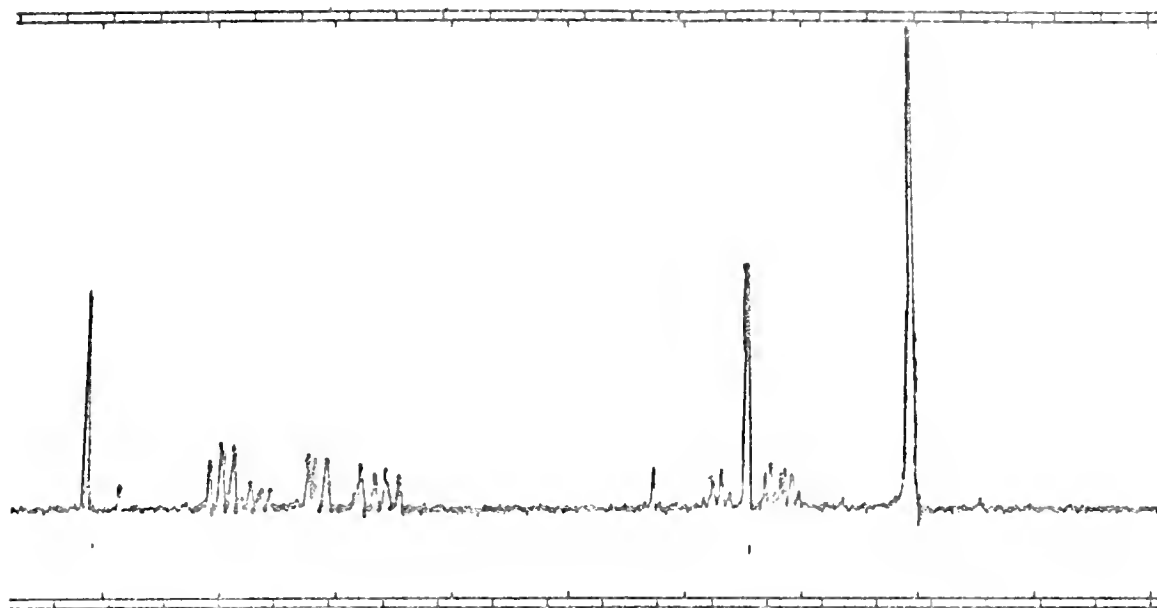
PROTON MAGNETIC RESONANCE SPECTRUM OF PRODUCT (33)



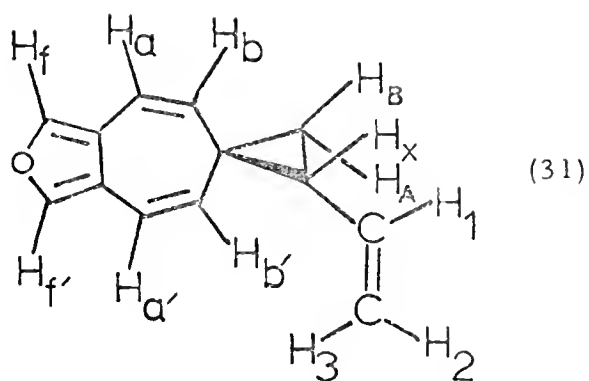
(Figure 34)

field doublet is two hydrogens. The integral for the upper-field doublet containing the signal for the cyclopentene olefinic hydrogens indicates a total of four hydrogens. The remainder of the spectrum is a sharp singlet at 7.49 tau with a correct integral for the four allylic hydrogens (H_d). The lack of discernible splitting of the allylic hydrogens is consistent with the reported 0.5 Hz. allylic splitting in cyclopentene itself.³³ The high symmetry of the 1,4-adduct (33) gives rise to some doubt as to whether the C=C bond in the cyclopentene ring should even be infrared active at all. Nevertheless, there is a weak absorption at 1618 cm.^{-1} that does fit the known pattern for C=C stretch in five-membered rings (cyclobutene, 1566 cm.^{-1} ; cyclopentene, 1611 cm.^{-1} ; cyclohexene, 1649 cm.^{-1}).³⁴

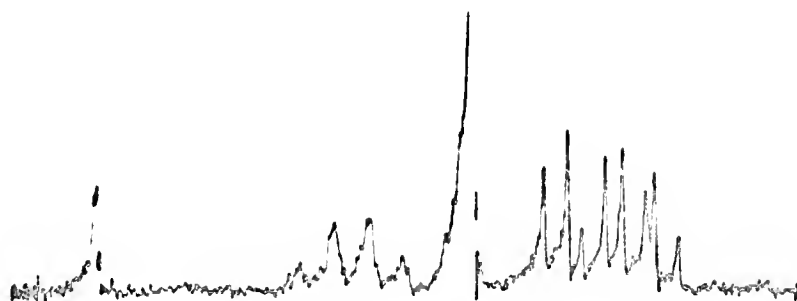
Structural assignment of the 1,2-addition product with butadiene was based on the following information. The furan hydrogens appeared as a two-hydrogen singlet at 2.9 tau. The vinyl region showed clearly the results of the symmetry-disturbing exocyclic vinyl group. The pattern for the (H_a) and ($H_{a'}$) hydrogens was a partially overlapping pair of doublets showing the same 11.5 Hz. coupling between the AB pair in the seven-membered ring that has been observed in (26) and (27). This four-line signal for the (H_a) and ($H_{a'}$) hydrogens was about 3.9-4.2 tau. Another four-line signal for the (H_b) and ($H_{b'}$) hydrogens appeared at about 5.1-5.65 tau. Once again, since these two hydrogens are nonequivalent, the W-form coupling of ca. 2 Hz. was observed in addition to the coupling with the (H_a) and ($H_{a'}$) hydrogens. The vinylic hydrogens belonging to the exocyclic vinyl group appeared between the two sets of signals for the AB pair in the seven-membered ring. The (H_1) signal appeared from about 4.2 to



PROTON MAGNETIC RESONANCE SPECTRUM OF PRODUCT (31)



(Figure 35)



PROTON MAGNETIC RESONANCE SPECTRUM OF PRODUCT (31)
SHOWING ENLARGEMENT OF ABX PORTION

(Figure 36)

4.45 tau with primarily a four-line pattern. The (H_2) and (H_3) hydrogens were at 4.75-5.0 tau presenting a complex pattern that had so much fine structure that direct measurement of the coupling constants was not possible. Use of a 100-MHz. spectrometer made it possible to resolve each set of vinylic hydrogens, both the AB pair and the exocyclic vinyl hydrogens, sufficiently to allow an accurate integration for each signal. All of the integrals were satisfactory. The remainder of the spectrum presented the expected ABX pattern for the cyclopropyl hydrogens. Direct measurement of J_{AB} was 5.0 Hz. The AB portion of the spectrum (for the vicinal cyclopropyl hydrogens) was at 8.6-9.0 tau. The X portion was at about 8.15-8.5 tau. The AB signal allowed easy recognition of the expected pair of overlapping quartets. The X signal gave an integral that was slightly lower than the correct value because some of the lines were buried in instrument noise. Four of the lines were visible, but only two of them were very strong. The spectrum also showed a sharp singlet at about 8.6 tau from a contaminating inhibitor (2,6-di-tert, butyl-4-methyl phenol) picked up during exposure of the sample to a commercial grade of tetrahydrofuran. Elemental analysis was made impossible because of the presence of the inhibitor, since it was difficult to separate from the sample. The problem was surmountable by the ready conversion of the 1,2-adduct to the 1,4-adduct (33), which was easy to separate from the inhibitor and to provide in pure form for elemental analysis. The exocyclic vinyl group in (31) was shown by infrared.³⁵

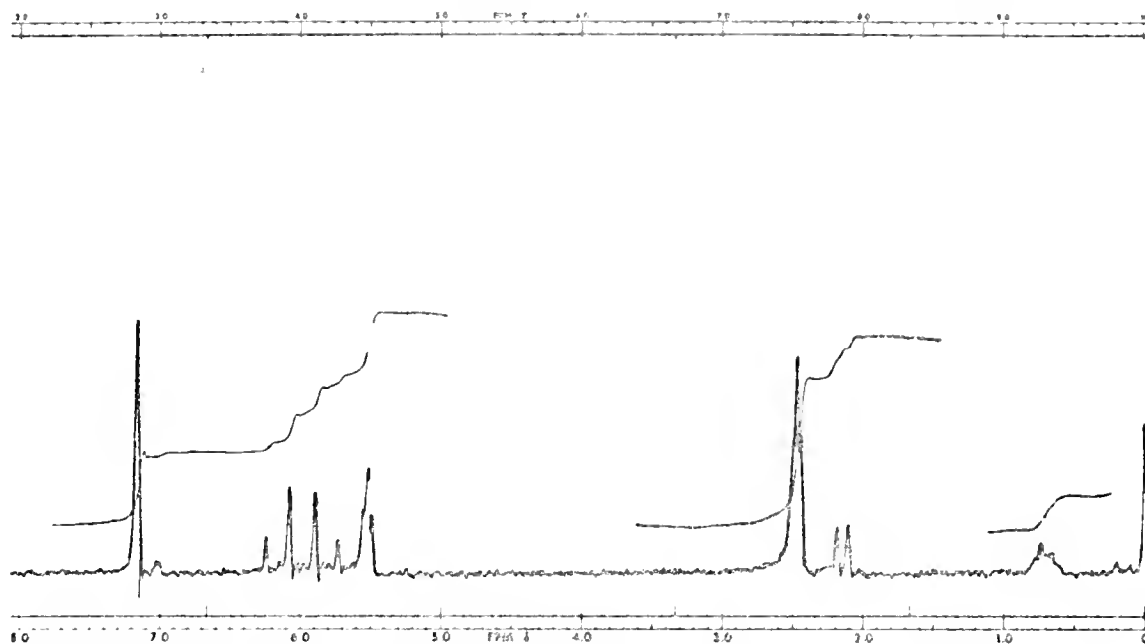
Decomposition of the tosylhydrazone salt by photolysis at low temperatures in the presence of 1,3-butadiene caused a remarkable

change in the character of reaction with this olefin. At temperatures of -60° to -30°C . it produces the product (40), shown in Figure 37, in about 40 percent yield as the only hydrocarbon product identifiable. The structure of (40) was identified by the striking similarities in its spectra with the spectra of a number of similar compounds recently prepared and elucidated in detail by Coburn.¹⁵ In the proton magnetic resonance spectrum the furan hydrogens produced a two-hydrogen singlet at 2.83 tau. The vinylic hydrogens (H_a) produced an AB pattern centered near 4.0 tau split by 10 Hz. The other vinylic hydrogens (H_b) produce a poorly resolved peak at 4.47 tau. The allylic hydrogens appear as a broadened peak at 7.52 tau. The cyclopropyl hydrogen (H_e) appears as a doublet at about 7.85 tau, coupled by about 5 Hz. to the other cyclopropyl hydrogen (H_i) which appears upfield as a multiplet at 9.15-9.45 tau.

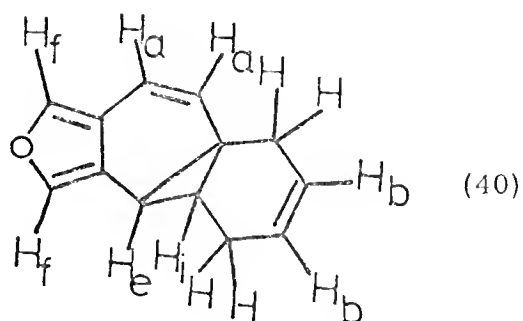
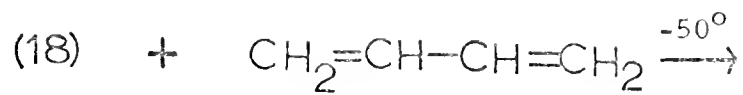
Photolysis of the tosylhydrazone salt at intermediate temperatures (ca. 40°C .) produced a mixture of (40) and the 1,2-addition product (31) from reaction with butadiene. The ratio was about 45:55. None of the 1,4-adduct (33) was produced.

In control experiments the 1,2-adduct (31) was shown to be stable to photolysis; therefore, it is not the source of the product (40). The product (40) was shown to be thermally stable for at least 20 minutes at 140°C ., since it could be purified by preparative gas chromatography.

To see if normal carbene behavior could be elicited at low temperatures, an effort was made to add the carbene to trans-2-butene by photolysis of the tosylhydrazone salt at -50°C . Normal carbene addition to the olefin did not occur, as shown by the proton



PROTON MAGNETIC RESONANCE SPECTRUM OF PRODUCT (40)



(Figure 37)

magnetic resonance spectrum of the crude product. The friable appearance of the product suggested that it was at least partly polymeric.

In experiments designed to allow equal amounts of olefin acceptors to compete for the carbene (11), the following relative rate data were obtained:

<u>OLEFIN</u>	<u>RELATIVE RATE</u>
1-butene	0.8
isobutene	1.0
1,3-butadiene	9.0

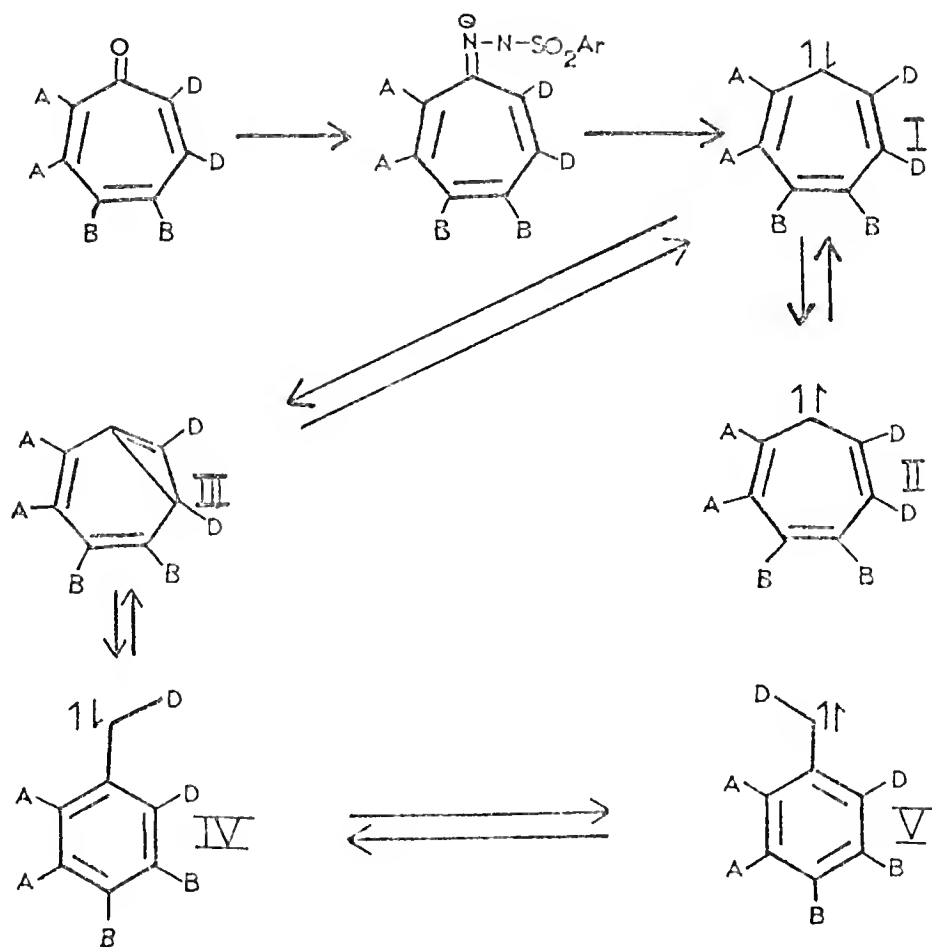
(Table 1)

One experiment was done to attempt to observe a signal in the proton magnetic resonance spectrum indicating the operation of the chemically induced dynamic nuclear polarization (CIDNP) phenomenon.³⁶ Such an observation would be indicative of the presence of a triplet carbene. Thermal decomposition of the tosylhydrazone salt in solution in an nmr sample tube containing a mixture of approximately 20 percent cyclohexene in d₆-dimethyl sulfoxide failed to show the CIDNP phenomenon. This could be attributable to the low solubility of the tosylhydrazone salt in this medium, indicated by the failure to observe the presence of the salt in the spectrum of the solution.

DISCUSSION

Thermolysis or photolysis of tosylhydrazone salts of tropone and substituted tropones in solution have been found to give at least five different kinds of reactive species (Figure 38). Unsubstituted tropone (12) shows chemistry of only the singlet carbene (I).^{1, 2, 9} Mono-annulated tropones (13) and (41) show some chemistry expected of the singlet carbene (I), but in general, their chemical behavior is dominated by the bicycloheptatriene (III) and the rearranged singlet and triplet aryl carbenes (IV) and (V).^{14, 20} The di-annulated tropone (42) shows only the chemistry of the bicycloheptatriene (III) and the aryl carbene, presumably singlet (IV) and triplet (V).¹⁵ The di-annulated and tri-annulated tropones (43) and (44) show typical diaryl carbene chemistry. They have been shown to have triplet ground states, but their chemistry is dominated by the singlet.^{10, 11, 12} The reasons for these differences can be qualitatively rationalized in terms of the expected relative energies of the different intermediates.

Carbene stabilities are thought to run parallel to cation stabilities. Mono-annulation, known to de-stabilize the tropylium cation, should not be expected to have significant effect on the stability of the intermediate cyclopropene (III). Mono-annulation should then decrease the stability of the carbene relative to the cyclopropene intermediate, making the rearrangement easier.²⁰ The di-annulated species (43) and the tri-annulated species (44), by incorporating into the fused benzene systems the double bond that must suffer attack in order for



- (12): A, B, D = H
 (13): A, D = H; B = fused benzene ring
 (41): A = fused benzene ring; B, D = H
 (42): A, B = fused benzene ring; D = H
 (43): A, D = fused benzene ring; B = H
 (44): A, B, D = fused benzene ring

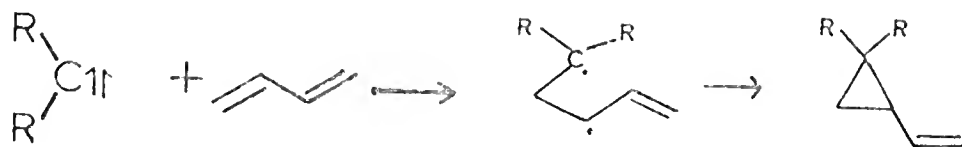
(Figure 38)

rearrangement to occur, reduce the probability of rearrangement by increasing the relative energy of the intermediate cyclopropene because of loss of benzenoid aromaticity. The di-annulated species (42) does not require as much loss of aromaticity to form the cyclopropene (III), so it undergoes rearrangement easily. Many carbenes that are formed in their singlet states react in their singlet states, because the singlet is so reactive that reaction occurs before collisional deactivation to triplet, if that is the ground state, can occur. Equilibration between a reactive singlet and a relatively unreactive triplet can also cause the same effect.

The present carbene (11) fits this overall scheme, but as a result of its unusual structure, it seems to have a unique place in the scheme. In the first place, unlike any of the other carbenes studied, under certain conditions (above about 40° C.) its chemistry is apparently dominated by the triplet.

The complete loss of stereospecificity in reactions of (4,5-c)furotropyliene is consistent with triplet behavior. The nonstereospecific addition of a carbene in solution is now well established as a criterion for interpreting the reaction in terms of a two-step reaction; i. e., via triplet. The present stereospecificity studies must be taken with the caveat of Gaspar and Hammond³⁷ in mind that "Nonstereospecific addition cannot be taken as a proof that an attacking species is a triplet unless it has also been shown that under some other conditions a species of the same composition can give stereospecific addition." Closs, in a more recent view, asserts that nonstereospecific reactions can always be interpreted as proceeding via the two-step mechanism; i. e., via triplet.²⁹

The relative reactivities of (4,5-c)furotropyliene in reactions with olefins also fit the triplet pattern. It is well accepted that conjugated dienes, such as 1,3-butadiene, show a high relative rate of reaction with triplets because of allylic stabilization of the di-radical intermediate (Figure 39) in the two-step reaction. The common use of butadiene as a "triplet scavenger" to improve stereospecificity of

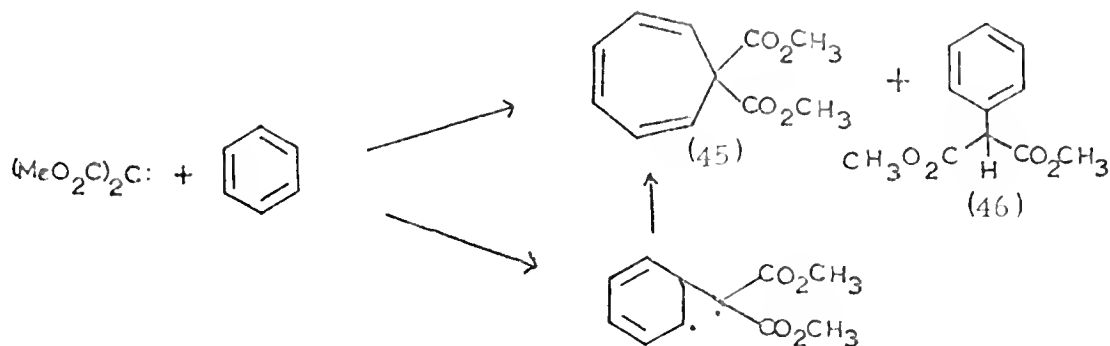


(Figure 39)

carbene reactions by selectively draining off triplet illustrates this principle.³⁸ The relative rates found in this present study also fit the relative rate pattern for the rate of radical addition vs. abstraction with the same olefins.³⁹

Interpreting the reaction of (4,5-c)furotropyliene with benzene in terms of triplet chemistry is aided by consideration of some related reports in the literature. Bis(carbomethoxy)carbene has been generated by photolysis of the corresponding diazo compound under two sets of conditions.³² Direct photolysis produces a carbene that reacts in the singlet state as shown by the stereospecificity of its reactions with olefins. Photosensitized decomposition produces a carbene that reacts in the triplet state as shown by the loss of stereospecificity in its reactions with olefins. The same carbene, prepared by each of the two methods, was allowed to react with benzene. Direct photolysis of methyldiazomalonate in benzene gave the cycloheptatriene (45) and

the C-H insertion product (46) in a ratio of 2.7 to 1.0. The photo-sensitized reaction gave the same two compounds in a ratio of 1.6 to



(Figure 40)

1.0. The increased amount of the phenylmalonate (49) when the carbene is prepared in the triplet state is consistent with the intermediacy of the di-radical, which can either close to the norcaradiene related to the cycloheptatriene, or undergo hydrogen shift to form the phenylmalonate. Increased triplet character in the attacking carbene increases the amount of the C-H insertion product. If the slow step of the reaction is attack of triplet carbene upon a benzene double bond, the absence of a deuterium isotope effect is to be expected. This was demonstrated in the present study with (4,5-c)furotropyliene.

Still, there are hazards in interpreting the insertion of furotropyliene into the C-H bonds of benzene as necessarily a triplet behavior. A di-radical intermediate such as that shown in Figure 40 could arise from another path. Consider, for example, the six-membered carbocyclic carbene, 4,4-dimethylcyclohexadienylidene. It apparently reacts with olefins in the singlet state in solution. It reacts with benzene to produce a spironorcaradiene (47) shown in Figure 41. This spironorcaradiene isomerizes at 100°C . to produce the intermediate (48) that is very much like the di-radical intermediate

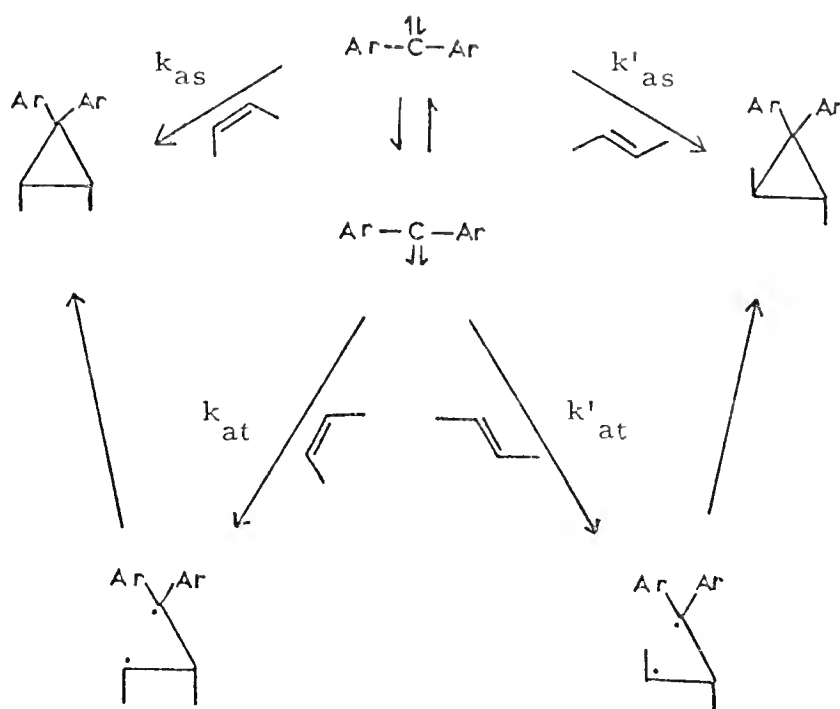
singlet state.^{17, 16} For example, direct irradiation of aliphatic alpha-diazoketones produces a predominance of the photochemical Wolff rearrangement; but photosensitized irradiation, which should increase triplet formation, produces an increased amount of cyclopropanes, suggesting normal intermolecular carbene reactions.¹⁷

Formation of the cyclopropene intermediate (16) is a particularly surprising result, since the (4,5-c)furotropyliene (11) has not shown any evidence of rearrangement to the isobenzofuran skeleton as might have been expected (Figure 11). This rearrangement, if it does occur, might be impossible to detect with certainty because of the high reactivity of the isobenzofuran molecule. It polymerizes rapidly in solution.²⁴ While one cannot say with certainty that none of the cyclopropene opens to the isobenzofuranyl carbene, the fact that yields of up to 50 percent of formal furotropyliene addition products are formed does allow one to say that the rearrangement is not the overwhelmingly predominant process such as is observed with the annelated cycloheptatrienylidenes (13), (41), and (42) in Figure 38. Perhaps the ring-opening of the cyclopropene intermediate (16) to the isobenzofuranyl carbene is precluded because not enough aromaticity is gained in that direction.

Why does triplet chemistry predominate in the reactions of furotropyliene at moderate to higher temperatures? The apparent ease of crossing from singlet to triplet suggests that these two electronic states are at very similar energy levels in this carbene. The effect of temperature in changing the character of the reactions of this carbene has a few interesting parallels in the literature.

Closs has reported a case in which there may be a temperature effect upon a singlet-triplet equilibrium.⁴⁰ Diphenyl carbene, known to have a triplet ground state, was produced by irradiation of diphenyldiazomethane in the presence of olefins. In reactions with cis- and trans-2-butenes, cyclopropanes account for no more than 10 percent of the hydrocarbon products. Hydrogen abstraction was the main reaction pathway. At -10°C. the cis- and trans-1,2-dimethyl-3,3-diphenylcyclopropanes were formed in a ratio of 3.2 from the cis-2-butene. The corresponding ratio from the trans olefin was 0.04. Lower temperatures caused increased stereospecificity. At -66°C. the product ratio from the cis-2-butene was 9.0. At a given temperature the product ratio was found to be independent of the butene concentration over a range of 150-fold dilution with cyclohexane. The presence of oxygen failed to change the isomer ratio of products. Closs postulated the following scheme (Figure 42) as a possible explanation of his observations. He suggested that intersystem crossing is much faster than any other reaction in the system and that the reverse crossing is also very fast so that both singlet and triplet are effectively in equilibrium. The relative rates of the singlet (k_{as}) and the triplet (k_{at}) addition steps and the position of the singlet-triplet equilibrium both determine the fraction of stereospecific singlet-state addition. Since diphenylmethylene is known to have a triplet ground state, the rate of crossing to the triplet (k_i) must be greater than the rate of triplet crossing to the singlet (k_{-i}); therefore, in view of the observed product ratios, the rate of singlet addition (k_{as}) must be much greater than the rate of triplet addition (k_{at}). If the difference in the free energies of activation for the two addition reactions is

larger than the free energy difference between the two electronic states, the temperature difference could be explained on this basis alone. It is not possible to determine whether a temperature effect upon the position of singlet-triplet equilibrium is being observed, but this is a possibility.



(Figure 42)

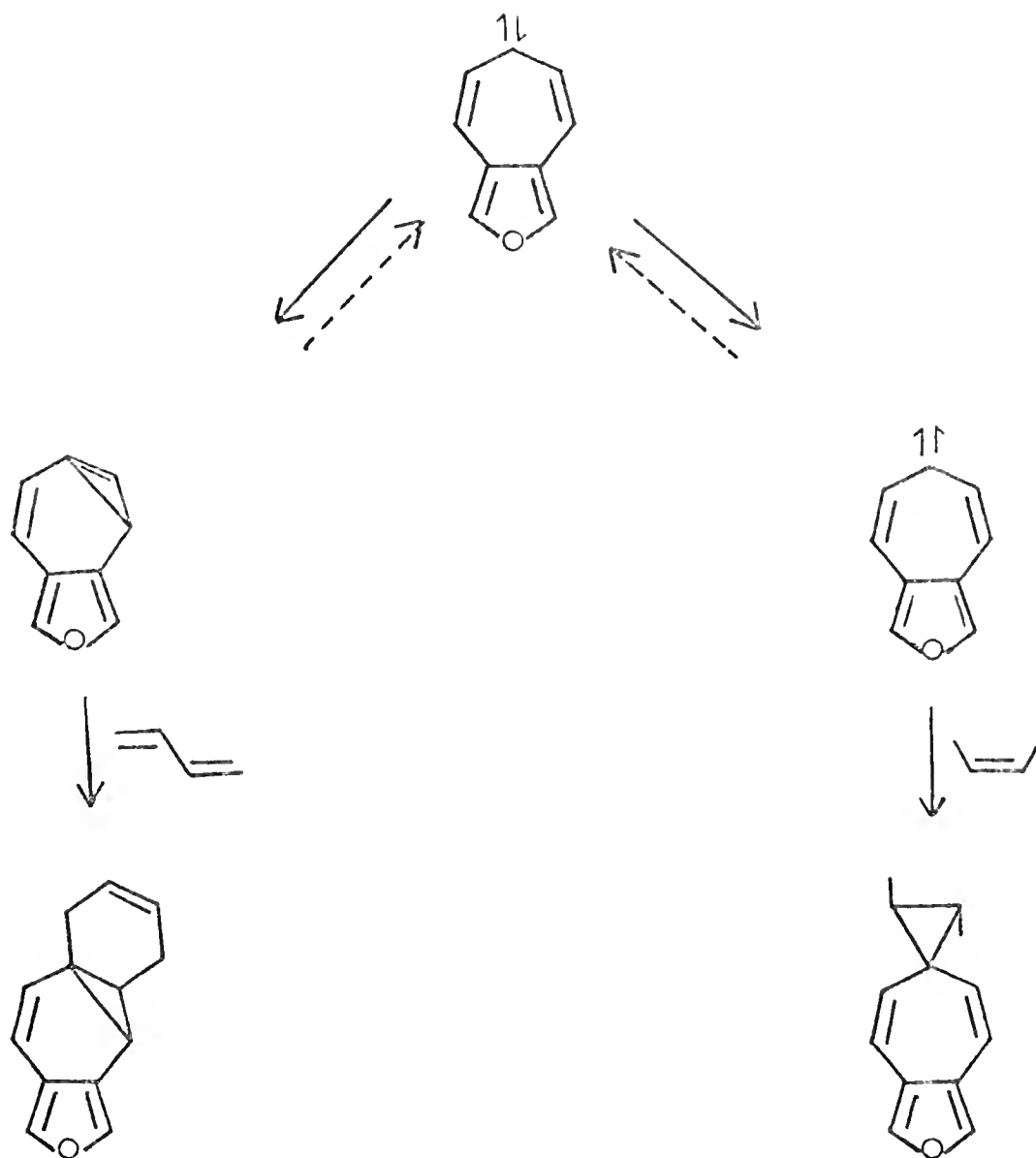
Thermal effects upon the population of electronic states are known in certain photochemically produced noncarbene species. An example is a study of pyrene-d₁₀ in a polymethylmethacrylate matrix.⁴¹ The triplet yield plus the fluorescence yield was near unity at -196°C. As the temperature was raised, two effects were observed. First, the triplet yield increased with increasing temperature, suggesting a temperature-dependent process that produces increasing intersystem

crossing from vibrationally excited singlet to second triplet state (T_2). The second effect observed was a falling off of the sum of triplet yield and fluorescence yield from the expected value of unity as temperature increased. This suggested a thermally dependent radiationless transition from the first singlet state to the ground state. The energy of activation for the temperature-dependent component of the intersystem-crossing process was determined to be about 2.6 kcal. per mole. The energy of activation for the radiationless transition from singlet to ground state was about 0.9 kcal per mole.

A somewhat similar study of 1,12 benzperylene has shown that, since the second excited singlet of this molecule lies only about 1300 cm.^{-1} (3.7 kcal. per mole) above the first excited singlet, there is significant thermal population of the second excited singlet state at 23°C .⁴²

Whether furotropyliene is showing a similar thermal effect upon population of electronic states is not possible to determine so long as the electronic states themselves cannot be observed except through their chemistry. This is because the relative rates of reaction of the electronic species with their trapping agents are unknown.

It is possible to draw several speculative schemes that could fit the presently known facts about (4,5-c)furotropyliene. Some of these are shown in abbreviated form in Figure 43. It seems reasonable to assume that the cyclopropene is lower in energy than the initially formed singlet carbene. The relative energies of the triplet and singlet states shown in Figure 43 can only be the subject of



(Figure 43)

speculation from the present data. It is interesting to consider the question as to whether equilibria exist between the species in Figure 39, but there is no experimental basis for a determination of this question. A hypothetical experiment can be devised to answer this question. If one can show that there is X percent formation of cyclopropene under a given set of conditions and that there is more than (100-X) percent of carbene addition observed under the same conditions in the absence of a cyclopropene trap, one could reasonably conclude that an equilibrium between cyclopropene and singlet carbene does exist. Such an experiment seems to call for extraordinarily high yields in these carbene reactions that are unlikely to be attainable. In all of these schemes it seems reasonable that singlet chemistry is not observed via intermolecular olefin trapping, since the intramolecular reaction to form the cyclopropene would be expected to be much faster than the intermolecular reaction.

It is interesting to speculate that perhaps triplet chemistry predominates at higher temperatures because the singlet, through its aromatic character, is relatively less reactive than triplet, and therefore has a sufficiently long lifetime to allow intersystem crossing to occur before singlet reaction occurs. An equilibration between singlet and triplet, with the triplet the more reactive of the pair, would also fit the data.

Perhaps the study of minor reaction products of (4,5-c)furotropylidene would shed additional light on these matters, but the separation and purification of such large molecules formed in such low yields presents formidable experimental difficulties.

EXPERIMENTAL

General. Melting points were taken in a Thomas-Hoover Unimelt apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Incorporated, Atlanta, Georgia. Accurate mass measurements were provided by Dr. R. W. King, using the MS-30 high-resolution mass spectrometer equipped with automatic data system, at the University of Florida. Infrared spectra were recorded on a Beckman IR-10 spectrophotometer. In all cases where the liquid film technique was not used, the KBr pellet technique was used. Nuclear magnetic resonance spectra were determined on a Varian A-60A high-resolution spectrometer, or in some cases, a Varian XL-100 instrument. Chemical shifts are reported in tau values from internal tetramethylsilane standard. Low resolution mass spectra were determined on a Hitachi RMU-6E mass spectrometer.

Analytical thin-layer chromatography was done on 2 in. x 8 in. plates coated in these laboratories with 0.25 mm. layers of E. Merck HF-254 silica gel; preparative work was conducted on 8 in. x 8 in. plates coated with 1.0 to 1.5 mm. layers of HP-254 silica gel. Components were visualized by their quenching of fluorescence under ultraviolet light. Analytical gas chromatography was accomplished with a Varian Aerograph Series 1200 flame ionization instrument using a 100-ft. capillary column coated with Ucon LB-550. Analytical results were obtained by planimetric measurement and by peak height times peak-width-at-half-height measurement.

All chemicals are reagent grade used as supplied unless otherwise stated. The furan-3,4-dicarboxylic acid was used as supplied by Aldrich Chemical Company, Milwaukee, Wisconsin. Solvents were dried by passage through a column of either freshly re-activated Linde Molecular Sieve (4A) or Woelm basic alumina, activity grade 0, followed by storage over calcium hydride under a nitrogen atmosphere.

3,4-Di(hydroxymethyl)furan. This compound has been reported as the product of the reduction of dimethyl-3,4-furandicarboxylate.²³ The reported yield of 76 percent did not result from use of the published procedure. The following procedure gave 72 percent conversion based on the diacid. A mixture of 31.2 g. (0.2 moles) 3,4-furandicarboxylic acid, 47.2 g. (0.4 moles) thionyl chloride, 200 ml. benzene, and 1 ml. N,N-dimethylformamide was heated at reflux for 1 hr. The reaction is essentially complete when all of the solid has dissolved. The benzene and excess thionyl chloride were removed in vacuum by rotary evaporator. The crude diacyl chloride, formed in essentially quantitative yield, was reduced directly without purification using the following procedure. The crude acid chloride was dissolved in ca. 300 ml. tetrahydrofuran. This solution was dripped into a stirred suspension of 30 g. lithium aluminum hydride in 800 ml. dry tetrahydrofuran. The mixture was stirred at room temperature overnight, then refluxed 8 hr. The reaction mixture was cooled. The excess hydride was destroyed by addition of about 300 ml. of 5 percent sodium hydroxide solution that had been saturated with sodium chloride. The ether layer was separated by decanting from the white granular slurry. This white residue was washed several times with diethyl ether. The washings were combined with the first (THF)

extract, washed with brine, dried with anhydrous MgSO_4 and filtered. Removal of the solvent on a rotary evaporator using aspirator vacuum gave 26.4 g. of crude 3,4-dihydroxymethylfuran. The product was identified by the correspondence of its spectral properties with the values reported in the literature.²³

3,4-Furandicarboxaldehyde. This compound was prepared from 3,4-di(hydroxymethyl)furan in two steps by the procedure of Cook and Forbes.²³ The first step, partial oxidation of the di-alcohol with activated manganese dioxide, gave yields of about 50 percent instead of the reported 80 percent. The best yields of dialdehyde were obtained by lead tetra-acetate oxidation of the crude 3-hydroxymethylfuran-4-carboxaldehyde containing about 50 percent of unreacted glycol, rather than by separation and purification of the mono-aldehyde. This procedure allowed the lead tetraacetate to oxidize, not only the mono-aldehyde in the mixture, but also the glycol that had not been oxidized by the manganese dioxide. This required use of about 50 percent more lead tetraacetate than would have been required for oxidation of an equal weight of 3-hydroxymethylfuran-4-carboxaldehyde to the dialdehyde. This procedure gave about 25 percent conversion of the glycol to 3,4-furandicarboxaldehyde. The produce was identified by the correspondence of its spectral properties and melting point with the values reported in the literature by Cook and Forbes.²³

(4,5-c)Furotropone. This compound was prepared by condensation of 3,4-furandicarboxaldehyde with acetone using the procedure of Cook and Forbes.²³ The yield and the physical and spectral properties of the product were exactly as reported.

(4,5-c)Furotropone tosylhydrazone. A solution of 2.0 g. (0.014 moles) p-toluenesulfonylhydrazine and a trace of phosphoric acid in 20 ml. of dry tetrahydrofuran was allowed to stand in a stoppered flask for three to seven days at room temperature. The solution was diluted with one volume of chloroform and allowed to stand in a refrigerator cabinet (ca. 5-7°C.) for 0.5 to 1 hr. The resulting slurry of crystals was poured onto a Buchner filter. The collected yellow crystals were washed with fresh chloroform on the filter. The combined wash solvent and mother liquor were eluted from a column of silica gel (4.5 x 15 cm.) using methylene chloride. The first (yellow) fraction was collected and evaporated to dryness. The residue was washed with chloroform and filtered. The resulting second crop of yellow crystals when combined with the first crop on the filter gave a total of 2.9 g. (66 percent conversion) of the ketone tosylhydrazone, m.p. 214-215°C. w. decomposition.

Anal. Calcd for $C_{16}H_{14}N_2O_3S$: C, 61.13; H, 4.49; N, 8.91.
Found: C, 60.97; H, 4.54; N, 8.85.

The spectral data were: ir (KBr, cm^{-1}) 3190, 1640, 1595, 1395, 1325, 1162, 1052, 930, 885, 830, 762, 680. nmr (d_6 -DMSO) 2.1 to 4.13 (complex pattern, total 10H), 7.62 (singlet, 3H).

(4,5-c)furotropone tosylhydrazone, sodium salt. A solution of 3.9 g. furotropone tosylhydrazone in 100 ml. dry tetrahydrofuran was stirred under dry nitrogen while 0.5 g. sodium hydride (washed with pentane) was added. After 0.5 to 1.0 hr. at room temperature, 50-75 ml. pentane was added to the reaction mixture. The resulting slurry of yellow solid was filtered in a dry nitrogen atmosphere (dry box) to recover 5.2 g. of the sodium salt.

Decomposition of tosylhydrazone salt in presence of benzene.

(4,5-c)Furotroponetosylhydrazone sodium salt (0.3 g., 0.7 mmole) was stirred with 50 ml. benzene in a sealed Fischer-Porter Aerosol Compatibility Test Tube (containing an atmosphere of dry nitrogen) and heated in an oil bath kept at 118°C . After 1 hr. the tube was cooled and opened. The dark brown slurry was taken from the tube and filtered through a sintered glass funnel. The solid filter cake weighed 0.24 g. The filtrate, upon evaporation of the benzene, left a residue of 0.14 g. This crude residue was chromatographed on preparative silica gel plates developed with hexane containing 5-10 percent benzene. The leading band of the chromatogram was collected, stripped from the adsorbent with ethanol, and recovered by evaporating the filtered solution. This resulted in collection of 0.063 g. of the benzene insertion product (25), m.p. $75-77^{\circ}\text{C}$.

Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{O}$: C, 86.49; H, 5.82. Found: C, 86.38; H, 5.85.

The spectral data were: ir (KBr, cm^{-1}) 1595, 1490, 1450, 1123, 1040, 872, 852, 800, 797, 762, 700; nmr (CDCl_3) 2.71 and 2.72 (two singlets, total 7H), 3.7 (complex, 2H), 4.5 (complex, 2H), 5.64 (complex, 1H); mass spectrum (70 eV) 208 (molecular ion), 131, 77.

Decomposition of tosylhydrazone salt in equimolar benzene- d_6 -benzene. A repeat of the above preparation in the presence of an equimolar mixture of benzene and hexadeuterated benzene produced a 50:50 mixture of the benzene insertion product and the deuterated benzene insertion product as determined by nmr (100 MHz.) and by mass spectroscopy.

Decomposition of tosylhydrazone salt in presence of styrene. A solution of 0.42 g. (4 mmoles) styrene in 15 ml. dry dioxane was heated to 100°C. in a flask equipped with thermometer, stirring bar, and an inlet for dry nitrogen. Dry solid tosylhydrazone salt (0.33 g., 0.8 mmoles) was added to the solution all at once. After 0.3 hr. the reaction mixture was quickly cooled in an ice bath as stirring was continued. The crude brown slurry in the flask was removed and filtered, then treated on a rotary evaporator to remove the dioxane and as much styrene as possible. The resulting residue was dissolved in chloroform and streaked on a preparative silica gel plate. Development of the plate in a mixture of hexane and chloroform gave 0.07 g. of somewhat impure spiro adduct in the major band. This material was purified by repetition of the silica gel chromatography using hexane as the solvent for development of the plate. This gave 0.06 g. of the oily liquid phenylspirocyclopropane (26), conversion 32 percent.

Anal. Calcd for $C_{17}H_{14}O$: C, 87.13; H, 6.03. Found: C, 86.81; H, 6.01.

The spectral data were: ir (film, cm^{-1}) 3130, 3080, 3060, 3020, 2995, 1662, 1600, 1540, 1495, 1450, 1410, 1210, 1125, 1047, 980, 875, 855, 815, 790, 698; nmr (CCl_4) 2.86 (singlet, 5H), 2.96 and 3.01 (two singlets, total 2H), 7.55-7.82 (complex, 1H), 8.5-8.76 (complex, 2H); mass spectrum (70eV) 234 (molecular ion), 216, 205, 191, 130, 128.

Thermal decomposition of tosylhydrazone salt in presence of trans-deuteriostyrene. The above preparation was repeated using trans-deuteriostyrene in place of styrene. Examination of the nmr

spectrum showed that the product consisted of equal parts of the cis and trans cyclopropanes. The spectrum showed a simplified ABX pattern as described in the text of this report.

Photolytic decomposition of tosylhydrazone salt in presence of trans-deuteriostyrene. A solution prepared as in the experiment above was irradiated in a sealed tube (magnetically stirred) with two Sears-Roebuck sunlamps at a distance of approximately 8-10 inches. During the reaction and the workup the product was not exposed to temperatures exceeding 50°C. The resulting phenylcyclopropane consisted of equal parts of the cis and trans products as shown by nmr.

Test of the thermal and photolytic stability of trans-deuteriostyrene. A small sample of trans-deuteriostyrene in an nmr sample tube was heated in a steam cone for 0.5 hr. The nmr spectrum was unchanged by the heating. The sample was also unchanged after it was irradiated by two Sears Roebuck sunlamps for 0.75 hr.

Decomposition of tosylhydrazone salt in presence of 1-butene. The salt (0.2 g., 0.48 mmoles) was heated with 5 g. 1-butene (liquid) that had been distilled into a Fisher-Porter Aerosol Compatibility Test Tube. The tube was kept in an oil bath at 110°C. for 1 hr. The excess 1-butene was then released. The crude residue was slurried with benzene and filtered through a sintered glass filter. The solid filter cake weighed 0.14 g. The crude filtrate left a residue of 0.05 g. after evaporation of the benzene. This residue (about 90 percent pure) afforded the ethyl spirocyclopropane (27) after purification by preparative vapor phase chromatography on an 8 ft. x 1/4 in. column packed with 60/80 mesh Anakrom ABS coated with 20 percent w/w SE-30.

Anal. High resolution mass spectroscopy (70 eV): Calcd for $C_{13}H_{14}O$: 186.1044. Found: 186.1036.

The spectral data were: ir (liquid film, cm^{-1}), 3145, 3070, 3035, 3000, 2975, 2940, 2880, 1670, 1540, 1470, 1460, 1132, 1050, 980, 880, 850, 810; nmr (CCl_4) δ 9.5 (singlet, 2H), 3.87-4.3 (overlapping doublets, total 2H), 5.25-5.8 (complex, 2H), 8.3-9.5 (complex, 8H); mass spectrum (70 eV) 186 (molecular ion), 171 ($C_{12}H_{11}O$), 158.07 ($C_{11}H_{10}O$), 157.06 ($C_{11}H_9O$), 144.05 ($C_{10}H_8O$), 130.04 (C_9H_6O).

Decomposition of tosylhydrazone salt in presence of isobutene.

The salt (0.3 g., 0.7 mmoles) was heated with ca. 4 g. liquid isobutene in a sealed Fisher-Porter Aerosol Compatibility Test Tube in an oil bath at $112^\circ C$. for 1-1.5 hr. The excess isobutene was then released to cool the contents of the tube. The crude residue that remained was slurried in benzene and filtered. The solid filter cake weighed 0.2 g. The filtrate, after evaporation of the benzene, weighed 0.038 g. Purification of this residue by taking the leading band on a thin-layer plate (silica gel) developed in hexane gave 0.017 g. of the purified dimethyl spirocyclopropane (28). The high purity of the crude product, as shown by its nmr spectrum, suggests that a large loss of material occurred during handling that was not attributable merely to purification.

Anal. High resolution mass spectroscopy (70 eV): Calcd for $C_{13}H_{14}O$: 186.1044. Found: 186.1060.

The spectral data were: ir (liquid film, cm^{-1}) 3055, 3030, 2980, 1770, 1725, 1540, 1440, 1365, 1130, 1110, 1050, 880, 825; nmr (CCl_4) δ 2.83 (singlet, 2H), 3.7-3.9 (doublet, 2H), 4.9-5.2

(doublet, 2H), 8.9 (singlet, 6H), 9.2 (singlet, 2H); mass spectrum (70 eV) 186.10 (molecular ion), 185.10 ($C_{13}H_{13}O$), 172.08 ($C_{12}H_{11}O$), 158.07 ($C_{11}H_{10}O$), 157.06 ($C_{11}H_9O$), 144.05 ($C_{10}H_8O$).

Thermal decomposition of tosylhydrazone salt in presence of cis- and trans-2-butenes. The same pyrolysis technique described above was used to decompose samples of the tosylhydrazone salt in the presence of cis- and trans-2-butenes. The resulting crude reaction mixtures had essentially identical nmr spectra and gas chromatograms (capillary column, Ucon LB-550). Pyrolysis of a 0.3-g. sample (0.72 mmoles) of the salt with 15 ml. liquid trans-2-butene at 118°C. produced a crude product weighing 0.09 g. Careful preparative layer chromatography (silica gel adsorbent, hexane solvent) of this material at low plate loadings gave 0.03 g. of trans-dimethylspirocyclopropane (34), 23 percent conversion.

Anal. High resolution mass spectroscopy (70 eV): Calcd for $C_{13}H_{14}O$: 186.1044. Found: 186.1052.

The spectral data were: ir (liquid film, cm^{-1}) 3030, 3000, 2960, 2935, 2855, 1665, 1540, 1455, 1387, 1130, 1088, 1050, 880, 810; nmr (CCl_4) 2.88 (singlet, 2H), 3.9 (doublet, 2H), 5.3 (doublet, 2H), 8.75-9.0 (three sharp peaks, total 6H), 9.0-9.5 (complex, 2H); mass spectrum (70 eV) 186.10 (molecular ion), 171.08 ($C_{12}H_{11}O$), 158.07 ($C_{11}H_{10}O$), 157.06 ($C_{11}H_9O$), 144.06 ($C_{10}H_8O$), 128.06 ($C_{10}H_8$).

Photolysis of tosylhydrazone salt in presence of cis-2-butene.

The photolytic decomposition of 0.33 g. tosylhydrazone salt with 12 g. cis-2-butene was carried out by irradiating the stirred slurry in a sealed tube for 1 hr. using two Sears-Roebuck sunlamps at a distance

of about 10-12 inches. This procedure produced a crude product mixture that gave an nmr spectrum and gas chromatogram that were essentially identical to those produced by the thermal decomposition of the salt in the presence of cis- and trans-2-butenes described above.

Photolysis of tosylhydrazone salt in presence of trans-2-butene at low temperature. Photolytic decomposition of 0.4 g. tosylhydrazone salt by irradiation for 1 hr. with a Hanovia 550-watt mercury lamp at a temperature of -30°C . produced a crude reaction mixture that contained no cyclopropane (34) as determined by nmr.

Determination of relative rates of reaction with various olefins. Relative rates of reaction with various olefins were determined using the pyrolysis method in a sealed tube as previously described. The temperature of the oil bath was kept at 118°C . for all runs. In each run a comparison of product formation from each of two olefins was done. Each olefin was present in equimolar amounts, measured by condensing equal volumes of the gaseous olefins into the reaction tube by use of a mercury-filled gas buret. The product ratios were determined by capillary column gas chromatography as described under the General heading of this section. The results are presented in Table I, page 31.

Pyrolysis with 1,3-butadiene at 110°C . Furotropone tosylhydrazone salt (0.25 g., 0.6 mmoles) was heated with ca. 20 ml. liquid 1,3-butadiene in a sealed Fisher-Porter Aerosol Compatibility Test Tube in an oil bath kept at 110°C . for 4 hr. Excess butadiene was vented to the atmosphere after the tube was removed from the bath and opened. The residue that remained in the tube was slurried in

benzene and filtered through sintered glass. The clear amber benzene solution was streaked on a preparative layer plate (silica gel) that was developed with hexane. The leading band of material gave 0.06 g. of the 1,4-adduct of butadiene (33), 55 percent yield. A small band of material following the 1,4-adduct was too small for identification.

Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.49; H, 6.65.

The spectral data were: ir (liquid film, cm^{-1}) 3060, 3020, 2930, 2850, 1618, 1540, 1440, 1340, 1132, 1052, 948, 882, 848, 800, 670; nmr (CCl_4) 2.82 (singlet, 2H), 3.8-4.7 (two doublets with overlapping signal, total 6H), 7.5 (singlet, 4H); mass spectrum (70 eV) 184 (molecular ion), 169, 155, 130, 129, 128, 54.

Pyrolysis with 1,3-butadiene at 100°C. The tosylhydrazone salt (0.36 g., 0.86 mmoles) was pyrolyzed with 1,3-butadiene by the above-described method using an oil bath temperature of 100°C. and reaction time of 0.5 hr. Similar workup and chromatography showed only a very weak leading band corresponding to the 1,4-adduct (33) (0.01 g.), followed by a second band that afforded 0.025 g. of the 1,2-adduct, the vinyl cyclopropane (31). A yield figure is not given in this reaction because the short reaction time and low temperature probably did not decompose all of the sodium salt.

Anal. Analysis was done by thermal isomerization of the 1,2-adduct to the known 1,4-adduct by heating it at 130°C. for 0.5 hr.

The spectral data were: ir (liquid film, cm^{-1}) 3140, 3090, 3010, 1542, 1217, 1132, 1052, 1000, 910, 880, 813, 790; nmr (CCl_4) 3.0 (singlet, 5H), 4-5.7 (complex, 7H), 8.2-9.1 (ABX pattern, 3H). An impurity gave a singlet at 8.64.

Photolysis of tosylhydrazone salt with 1,3-butadiene at low temperature. The tosylhydrazone salt (0.4 g., 0.98 mmoles) was photolyzed in a stirred reactor at -40° to -50°C . using the Hanovia 550-watt lamp for 2 hr. Workup, including thin-layer chromatography, as described before afforded 0.07 g. of the Diels-Alder adduct (40), 39 percent conversion.

Anal. High resolution mass spectroscopy (70 eV): Calcd for $\text{C}_{13}\text{H}_{12}\text{O}$: 184.0887. Found: 184.0880.

The spectral data were: ir (liquid film, cm^{-1}), 3040, 2960, 2880, 2840, 1630, 1430, 1280, 1220, 1050, 1110, 1025, 892, 860, 780, 740; nmr (CCl_4) 2.83 (singlet, 2H), 4.0 (doublet, 2H), 4.47 (broad, 2H), 7.52 (broad, 4H), 7.85 (doublet, 1H), 9.15-9.45 (multiplet, 1H); mass spectrum (70 eV) 184.0887 (molecular ion), 182.073 ($\text{C}_{13}\text{H}_{10}\text{O}$), 169.065 ($\text{C}_{12}\text{H}_9\text{O}$), 168.057 ($\text{C}_{12}\text{H}_8\text{O}$), 165.070 ($\text{C}_{13}\text{H}_9\text{O}$).

Photolytic stability of vinylcyclopropane (31). A sample of the vinylcyclopropane (31) was irradiated with two Sears-Roebuck sun-lamps for 0.5-0.75 hr. It was unchanged after irradiation.

Photolysis of tosylhydrazone salt with 1,3-butadiene at 40°C . A small-scale photolysis (ca. 25 mg. salt) was run in the presence of 1,3-butadiene at 40°C . The product ratio was determined by a gas chromatographic analysis (see General heading) of the crude product, followed by another similar analysis after removal of all 1,2-adduct by thin-layer chromatography. The result showed that the Diels-Alder adduct (40) and the vinylcyclopropane (31) were present in a 45:55 ratio with none of the 1,4-adduct (33) present.

CIDNP Experiment. A saturated solution of the tosylhydrazone salt in an nmr tube containing a solution of ca. 20 percent cyclohexene in d_6 -DMSO was heated in the variable temperature probe of the Varian A-60A at 120° C. for 10 min. No change in the spectrum was detected before, during, and after heating.

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BIOGRAPHICAL SKETCH

Thomas Howard Ledford was born August 24, 1942, in Macon, Georgia, to Mr. and Mrs. Howard William Ledford. He was graduated from Swainsboro High School, Swainsboro, Georgia, in 1960 and entered the University of Georgia as a four-year General Motors Scholar that September. While there he was elected to Phi Beta Kappa and received the Merck Award and the American Institute of Chemists Award. He obtained the degree of Bachelor of Science in Chemistry in June, 1964. The period 1965-1968 was spent in industrial research in organic chemistry with Tennessee Eastman Company, Kingsport, Tennessee. In 1968 he enrolled in the Graduate School of the University of Florida with a Woodrow Wilson National Fellowship. He was also a Graduate School Fellow during his graduate study. He is a member of the American Chemical Society and Phi Beta Kappa.

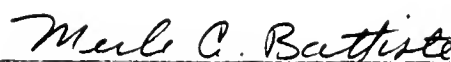
Mr. Ledford is married to the former Joan McDaniel of Oneonta, Alabama. He will be working for the Esso Research Laboratories of Exxon, U.S.A., in Baton Rouge, Louisiana.

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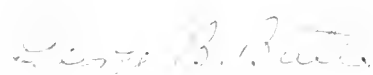
William M. Jones
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Merle A. Battiste
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George B. Butler
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Roger G. Bates
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

A handwritten signature in dark ink, appearing to read "Richard H. Hammer", is written over a horizontal line.

Richard H. Hammer
Associate Professor of Pharmaceu-
tical Chemistry

This dissertation was submitted to the Department of Chemistry in the College of Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August, 1973

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